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MECHANICAL TREATMENT OF FLY ASHES. PART I: PHYSICO-CHEMICAL CHARACTERIZATION OF GROUND FLY ASHES

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ABSTRACT

Physico-chemical characteristics of mechanically treated fly ashes are investigated. An original fly ash was ground, using a laboratory mill, for several times (from 10 to 60 minutes). Respect to physical characterization, fineness increasing of samples with grinding time was observed, but loss of effectiveness occurred for grinding time longer than 20 minutes. Ground samples showed higher specific gravity probably due to the presence of cenospheres in the original fly ash. Only a little change in mineralogical composition of fly ashes was observed when grinding: calcium carbonate formation by reaction of calcium oxide with carbon dioxide. Chemical behavior (pH and conductivity) of fly ash/water suspensions were studied and acid neutralization capacities measured.

Introduction

Research on the role of fly ashes in pastes, mortars and concretes has been widely reported, and a lot of studies on fly ash/Portland cement mixture properties have been in detail tackled. So, it is generally accepted that: a) shape morphology and size of fly ash particles strongly affect the properties of freshly mixed pastes, mortars and concretes, due to lubricant and filler effect; and b) chemical composition, vitreous character and specific surface of fly ash samples specially contribute to modify hardened paste, mortar and concrete properties, due to pozzolanic reaction with calcium hydroxide produced during cement hydration process.

Properties of fly ashes could be modified by means several procedures being the most frequently-used ones the classification of a original fly ash in several fractions with different fineness (sieving (1), flotation or air classification (2-5)), and collection from successive precipitation steps (4,6,7) (mechanical and electrostatic separators) in the thermoelectric power plant. In both cases, removal of coarse particles improves fly ash quality, due to the most of less-reactive and irregular shaped particles are separated; so, for processed samples, increasing of fineness is observed and spherical or spheroidal shape morphology of particles is maintained.

Grinding is an alternative processing method (5,7,8) for increasing fineness of a fly ash, although typical morphology of particles is substantially modified.

Physico-chemical characterization of processed samples of a fly ash may be the first step before the study if their adequate use for improving fly ash/Portland cement mixtures or for promoting new "directions for use" of these materials.

This paper reports on results of investigation to compare physico-chemical characteristics of ground fly ashes with original fly ash or their classified fractions. And, additionally, starting from data obtained, their influence on mortar cement/fly ash mixtures will be discussed.

Experimental Section

Materials: An original low-calcium fly ash (class F according to ASTM C-618) from thermoelectric power plant of Andorra-Teruel (Spain) was used as received. Analytical data (dry sample): LOI 2.44 %; Fe_2O_3 16.0 %; Al_2O_3 26.2 %; SiO_2 41.4 %; CaO 6.1 %; MgO 1.1 %; Na_2O 0.1 %; K_2O 0.5 %. Toluene (Panreac) for specific gravity determination and calcium carbonate (Merck) for carbonate content determination were analytical grade and used as received.

Apparatus and Procedures. Samples of original fly ash (namely T0) were ground using a laboratory ball-mill (Gabbrielli Mill-2) for several times: 450 g of T0 fly ash were introduced into the bottle-mill containing 98 balls of alumina (2 cm diameter) and were ground during 10, 20, 30, 40 and 60 minutes yielding the ground fly ashes T10, T20, T30, T40 and T60 respectively.

Infrared spectra were recorded on a Perkin Elmer 781 Spectrophotometer as KBr pellets. Granulometric distributions were performed using Sympatec Helos Analyzer. X-ray powder diffractogramms were recorded on a XRPD Siemens D-500 using nickel-filtered Cu-Kα radiation at 40 kV and 20 mA. Microphotographs by scanning electron microscopy (SEM) (ISI-DS-130) with energy dispersive X-ray (EDX) model (Kevex 8000) were performed on samples with 20 kV accelerating voltage. The thermal behavior of fly ashes was studied by TG and DSC (9) with Netzsch Simultaneous thermal Analyzer STA 409 between 20 ºC and 1100 ºC at a heating rate of 10 K/min, in a platinum crucible in air with a flow rate of 100 cm^3/min and using calcined kaolinite as reference. Blaine air permeability apparatus was used for determining fineness of fly ash samples as ASTM C-204 indicates, and density of fly ashes were determined using standard Le Chatelier flask as ASTM C-188 indicates. Carbonate content was determined using a Bascomb Calcimeter (10) (manometric method). WTW LF92 conductimeter with incorporated thermometer and compensation mechanism and Crison pH/mV-meter 501 were used for conductivity and pH measurements respectively.

Results and Discussion

Physical Characteristics: Most common physical properties which are usually determined on fly ashes, as granulometric distribution and fineness, specific gravity and particle shape morphology, have been studied. Several parameters related to the above mentioned properties are given in Table 1.

TABLE 1. Granulometric and fineness parameters for ground fly ashes.

Fly ash	Mean diameter d_m * (µm)	Median diameter d_{50} (µm)	Specific gravity ρ (g/cm^3)	S_v † (m^2/cm^3)	S_m † (cm^2/g)	S_b † (cm^2/g)
T0	32.19 (3.62)	15.64	2.44	0.971	3980	2810
T10	13.48 (1.44)	7.86	2.60	1.620	6230	3560
T20	9.96 (1.03)	6.00	2.68	1.871	6980	4320
T30	8.49 (0.86)	5.21	2.65	1.975	7450	4860
T40	6.91 (0.69)	4.13	2.64	2.245	8500	4930
T60	5.93 (0.57)	3.58	2.69	2.403	8930	5670

* Standard deviation values are given in parentheses

† Specific surface: S_v and S_m are calculated surfaces per volume unit and per mass unit respectively; S_b represents Blaine fineness

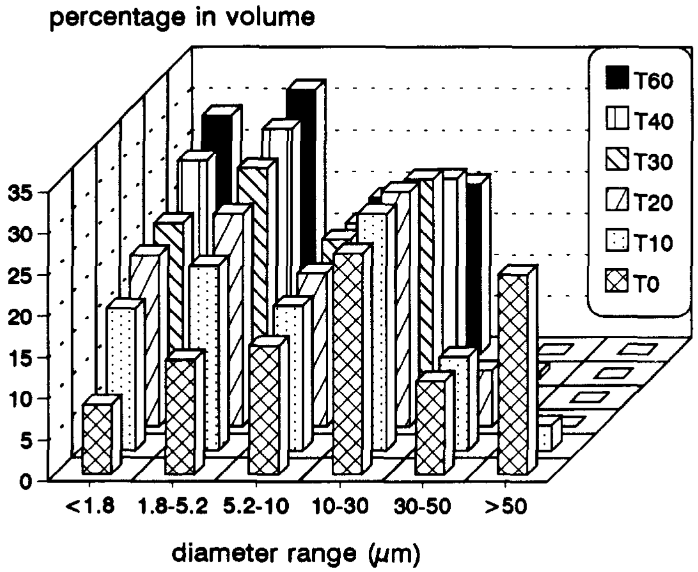

FIG. 1.
"Evolution" of granulometric distribution of fly ashes with grinding time.

These data revealed that for short grinding times (T10 and T20 samples) mean diameter, d_m, and median diameter, d_{50}, were drastically reduced; however, a grinding effectiveness loss is observed: for longer grinding-time only little diminution of mean particle diameter was observed. Figure 1 shows the "evolution" of granulometric distribution with grinding-time. In few minutes, the majority of particles with diameter greater than 50 μm have been crushed and, for grinding-time longer than 30 minutes, the percentage of particles greater than 30 μm is negligible. On the other hand, it can be noticed that percentage of particles less than 5.20 μm undergoes a noteworthy increase with grinding-time. Medium size particle percentages 5.20 to 30 μm were maintained during grinding.

During the milling process an increase of specific gravity, ρ, has been observed; for T10 sample, specific gravity increased in 0.16 g/cm^3 respect to original T0 fly ash. A little increase until 2.69 g/cm^3 is observed with grinding-time. Starting from these data, we can conclude that: a) greater particles, which are crushed easier, present lower density that finer particles; probably part of them are hollow spherical particles (cenospheres); b) carbon particles, which usually presents high porosity and low specific gravity values, and due to their softness, are converted in smaller particles with lower porousness.

In order to estimate qualitatively both contributions to increase specific gravity, samples of T0, T10 and T60 fly ashes were calcined at 800 ºC during 30 minutes; specific gravity values were 2.56, 2.68 and 2.75 g/cm^3 respectively, indicating that, in a way, carbon burning influence on increasing specific gravity overcoat on T0 sample where carbon presents higher porosity. On the other hand, original T0 fly ash was sieved using No. 270 (53 μm) ASTM sieve; the retained fraction (about 25 %) presented higher loss on ignition value (3.86 %) than original fly ash (2.44 %) and its specific gravity being 2.32 g/cm^3, value notably less than 2.44 g/cm^3 for T0, indicating that coarsest fraction of fly ash contributes to yield lower specific gravity values.

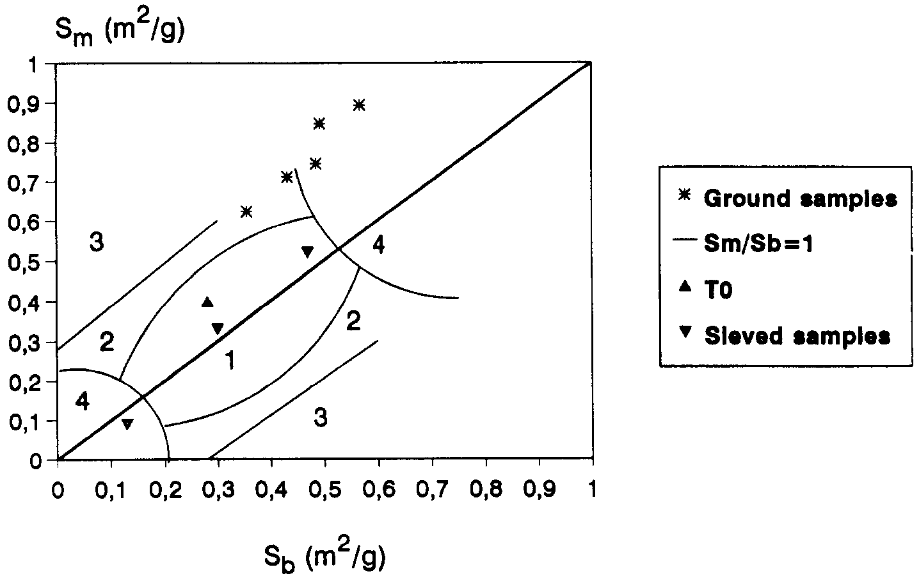

FIG. 2.

Zoned chart for the "shape factor parameter" and data for original, ground and sieving classified fly ashes.

Table 1 shows specific surface area of ground samples calculated from granulometric data (units of surface area contained in a unit of volume, S_v, and units of surface area contained in a unit of mass, S_m) and determined by the Blaine method, S_b. It can be distinctly noticed that S_m values are always greater than S_b; however, ground samples showed S_m/S_b ratio much more greater than for original T0 one, indicating that in the grinding process particles become less spherical, and so, reducing, in a way, their potential use as water reducing addition in mortar and concrete mixes (11). Correlation between S_m and S_b, and, moreover, a zoned chart for shape factor classification (11) are depicted in Figure 2. From workability point of view, ashes sited in zone 1 are the most beneficial for use in cement mixes. Progressing from zone 1 outwards, ashes becomes less useful to reduce the water content in cement mixes. Comparing data for ground samples and for sieving classified samples it can be concluded that for "non-destructive" methods, shape factor is clearly maintained.

Finally, grinding effect on shape morphology has been studied by SEM. A closer examination of ground samples reveals evidence of crushed particles; Figure 3 shows a wide range of morphologies. Plate 3a shows a general panorama of ground sample where non-altered spherical particles present diameter less than 20 μm; very irregular particles with 40 μm diameter and also a lot of very little particles can be observed. Plate 3b shows a high amount

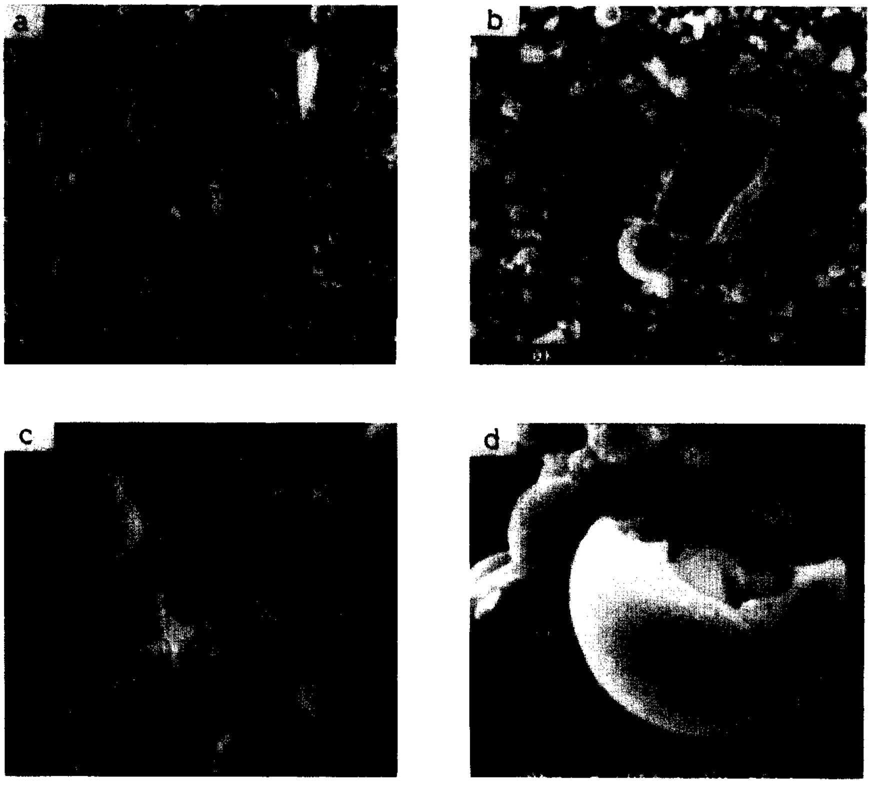

FIG. 3.

Ground fly ash SEM microphotographs: a) and b) general panorama of ground samples; c) large magnification of solid crushed particle; d) large magnification of "open" cenosphere.

of little particles and two very different morphologies of 5–10 μm diameter particles; moreover, irregular particle presented an "open" hole into the mass, which has been filled with small fragments. Plate 3c shows a large magnification of a crushed particle with "eighth part of sphere" shape, and plate 3d an "open" cenosphere which appeared to have filled with small spheres (plerospheres).

Mineralogical characteristics: After grinding of a fly ash, its chemical and mineralogical composition may remains unchanged. T0 and T60 fly ashes presented typical peaks in the X-ray diffractogram corresponding to fly ash with low lime content (12): quartz (Q), mullite (Mu), hematite (He) and magnetite (Ma) are present as a major crystalline components. Calcium carbonate (CC) appeared in trace amounts but no evident differences are observed between T0 and T60 samples probably due to background level.

Infrared spectroscopy permits to discover the inequalities which also exists in non-crystalline phases of fly ashes. Figure 4 shows infrared spectra for some samples and some chemically treated samples. A main and very broad absorption zone appeared centered at 1100 cm^{-1}, corresponding to a Si–O stretching vibration mode (12,13) from vitreous and crystalline silicon dioxide and silicates. T0 presented (Figure 4, "a" spectrum) additionally, other two resonances with lower intensity: the first peak centered at 1640 cm^{-1} which can be attributed to the presence of little amounts of water present in KBr used (H–O–H bending motion); the second one, a shoulder of main signal about 1430 cm^{-1}. When original fly ash T0 is ground, intensity increasing of signal centered at 1430 cm^{-1} is observed (Figure 4, "c" and "d" spectra). Signal at 1430 cm^{-1} can be attributed to a vibration mode of carbonate anion (CO_3^{2-}) which is a high intensity signal (13). Moreover, when T0 sample was left to atmospheric

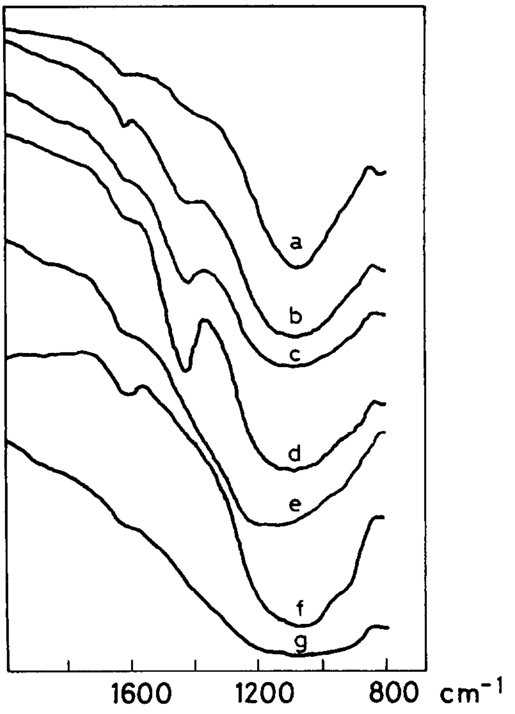

FIG. 4
Infrared spectra:
a) T0 fly ash; b) T0 left to atmospheric conditions during 1 year; c) T10 fly ash; d) T60 fly ash; e) T60 treated with hydrochloric acid and dried to 110 ºC; f) T0 calcined at 800 ºC and ground for 10 minutes; g) T60 calcined at 800 ºC

conditions also an increasing of this signal was observed (Figure 4, "b" spectra"). This fact indicates that carbonate anion infrared resonance appeared as consequence of calcium carbonate formation from free lime and carbon dioxide:

$$CaO + CO_2 \Rightarrow CaCO_3$$

For verifying the nature of this component, ground samples were treated with hydrochloric acid (CO_2 evolution was observed) and calcined at 800 ºC (calcium carbonate decomposition). Infrared spectra of these treated samples (Figure 4, "e" and "g" spectra) revealed a complete lack of carbonate absorption. But, what is the source of carbon dioxide into the bottle mill? The atmospheric CO_2 content into the bottle mill is not enough for producing the observed amounts of calcium carbonate. Probably, the source of CO_2 is the combustion of carbon particles, which are pulverized in thin and very reactive layers, and, subsequently, reacts with free lime:

$$C + O_2 + CaO \Rightarrow CaCO_3$$

The role of carbon particles is checked by calcination (removing carbon) of T0 sample and following grinding. Infrared spectrum (Figure 4, "f" spectrum) do not show absorption in 1340 cm^{-1} zone, indicating that presence of carbon is essential for producing, finally, calcium carbonate. It can be noticed that $CaCO_3$ content markedly increases when sample is ground, and, consequently, loss on ignition value also increases (Table 2).

TABLE 2. Moisture, loss on ignition and $CaCO_3$ percentages of fly ashes

Sample	Moisture (%)	Loss on ignition (%)	$CaCO_3$ (%)
T0	0.15	2.44	1.79
T10	0.24	2.65	2.60
T20	0.27	2.69	2.63
T30	0.30	2.66	2.60
T40	0.27	2.74	2.68
T60	0.25	2.81	2.84

Another little change in mineralogical composition was observed in ground samples. When mechanically treated samples reacted with hydrochloric acid, hydrogen sulphide was detected using a filter paper, moistured with a solution of lead acetate, on the mouth of the tube test (14) (a blackening of the paper indicated a sulphide anion in the sample). The source of sulphide in ground sample can be due to the reduction of little amounts of sulphate with carbon, as following chemical equation (15):

$$SO_4^{2-} + 4\ C \Rightarrow S^{2-} + 4\ CO$$

Attempts for quantifying sulphide content were unsuccessful.

Finally, thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis (9) were carried out and respective curves for T0 and T60 samples are plotted in Figure 5.

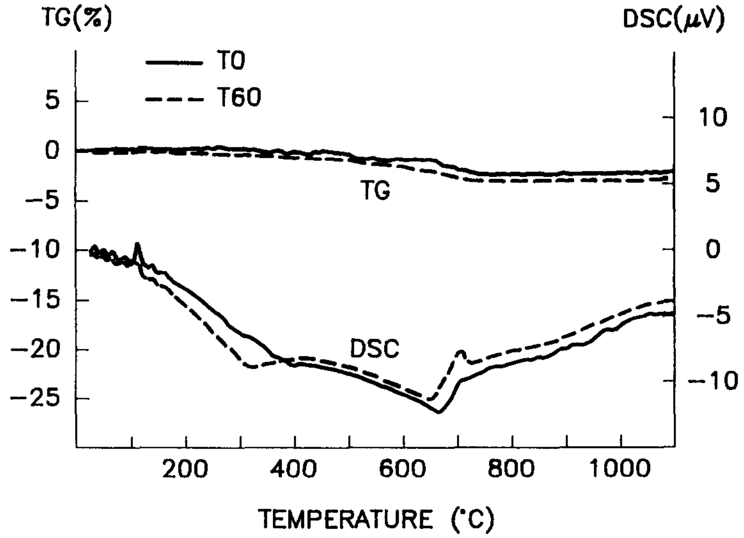

FIG. 5
TG and DSC curves for T0 and T60 samples.

Thermogravimetric data for both samples revealed a decreasing of mass from, approximately, 500 ºC to 800 ºC, due to carbon combustion and $CaCO_3$ decomposition. With regard to DSC data, we can notice that a first peak appeared at low temperatures, which can be attributed to a structural changes; this process is favored at lower temperatures for ground sample (324 ºC) compared to original fly ash (399 ºC) because, probably, fineness of sample. At higher temperatures, another peak about 660-670 ºC appeared (attributed to carbon burning) and, only for ground sample, a low intensity signal is showed at 727 ºC (probably due to higher amounts of calcium carbonate).

Chemical Characteristics: In first studies fly ash chemical characteristics were tested studying their behavior in water and their reactivity towards acid conditions. Conductivity and pH of suspensions prepared mixing 10 g of fly ash and 100 mL of distilled water were measured.

Figures 6 and 7 represent the evolution of conductivity and pH values during time, carried out at a liquid solid ratio (L/S) of 10; in both plots, it can be noticed that ground samples reacted more rapidly with water because of largest specific surface but for long time data no significant difference is observed among original and ground samples.

Reactivity of fly ashes towards hydrochloric acid (see Figure 8) demonstrates that ground fly ashes showed higher acid neutralization capacity (ANC); this alkaline behavior clearly appeared for low grinding-time (T10) and increasing grinding-time slightly raises alkalinity. Further studies on chemical behaviour of fly ashes are being carried out and additional information will be provided.

Conclusions

1- Fly ash particles with diameter greater than 30 μm were easily crushed using a laboratory

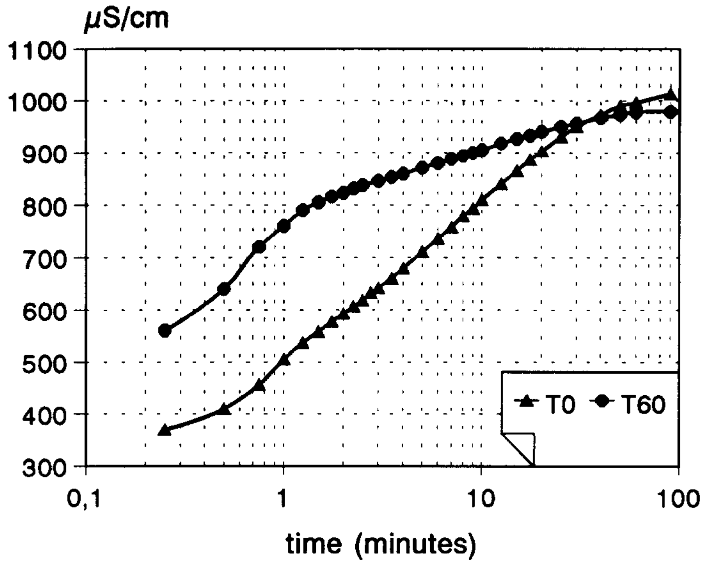

FIG. 6
Conductivity vs. time for aqueous suspension of fly ashes (L/S = 10 l/Kg)

mill, and samples with mean diameter of particles less than 10 μm were obtained for grinding time equal or longer than 20 minutes.

2- Ground samples showed specific gravity values greater than original fly ash because crushing cenospheres and porous carbon particles.

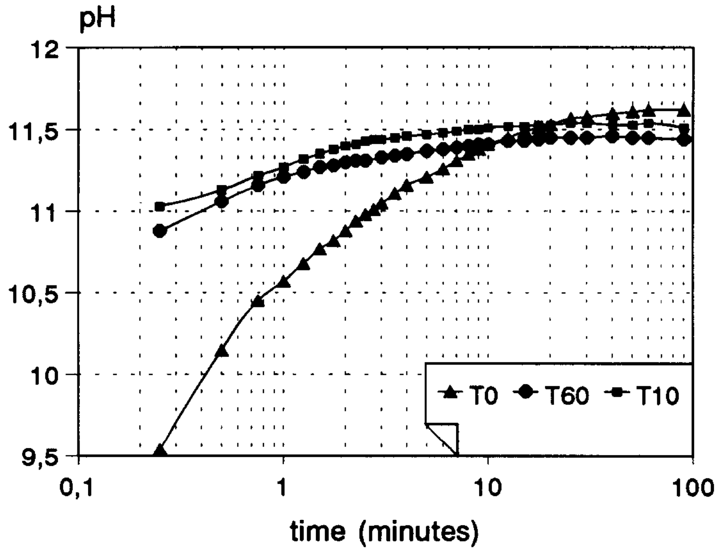

FIG. 7
pH vs. time for aqueous suspension of fly ashes (L/S = 10 l/Kg).

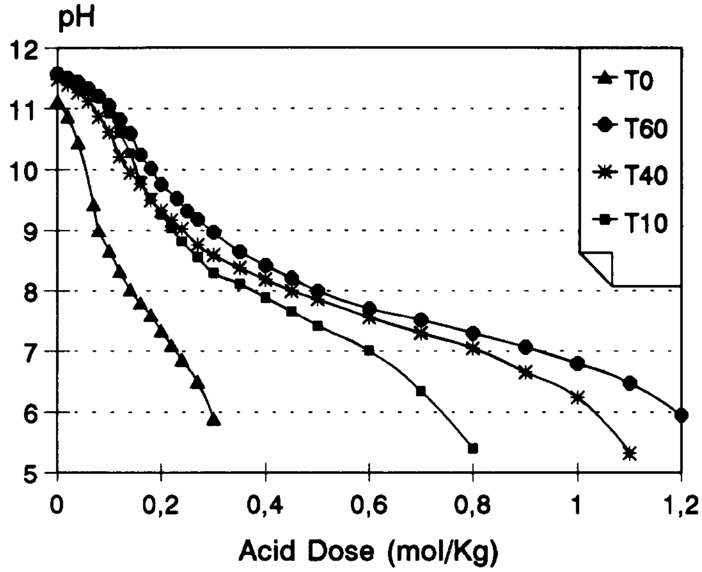

FIG. 8
pH in function of acid dose (L/S = 25 l/Kg)

3- Grinding strongly affected shape morphology of fly ash particles and samples became, potentially, less suitable as water reducing agents.

4- Increasing of specific surface values when grinding could modify pozzolanic reaction rate with lime and would produce an enhancement in early and long-term strength development.

5- Grinding process produced an increasing of calcium carbonate content in fly ashes, due to partial combustion of carbon particles and following reaction with calcium oxide. Little amounts of sulphide also were detected.

6- Increasing fineness was observed when grinding, and ground samples showed greater reactivity towards water and higher acid neutralization capacity.

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