POZZOLANIC PROPERTIES OF INCINERATOR BOTTOM ASHES AND THEIR EFFECT IN LIME PASTES

Radson L. Figueiredo* and Sara Pavía*

* Department of Civil, Structural and Environmental Engineering, Trinity College Dublin
e-mails: limafigr@tcd.ie, pavias@tcd.ie

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Abstract. *Pozzolans enhance hardening and strength of hydrated-lime mortars. They accelerate hardening and increase ultimate strength by imparting a hydraulic set often still preserving their physical and chemical compatibility with traditional and historic masonry. This paper assesses the activity of a number of incineration bottom ashes (IBAs) in order to evaluate their potential as pozzolanic additions in lime mortars. The progressive reduction of electrical conductivity of a lime-saturated solution evidenced that all ashes consumed lime thus exhibiting activity. The Scanning Electron Microscope (SEM) showed a high specific surface and a wide particle size distribution agreeing with the high specific surface area measured by gas adsorption. The reactivity of the ashes was further proven by monitoring the compressive strength development of lime: IBA mixes in relation to a standard lime mix over 90 days. The strength values, reaching up to 1,67 and 0.57 N/mm² for compressive and flexural strength respectively, compare with typical values reached by feebly hydraulic limes, further supporting pozzolanic activity.*

1 INTRODUCTION

It has been known since antiquity that the hardening, strength development and ultimate strength of hydrated-lime mortars ($Ca(OH)_2$; European designation CL- Calcium lime) can be enhanced using pozzolanic materials. In many instances, pozzolans enhance lime mortars while still preserving their physical and chemical compatibility with traditional and historic masonry.

Pozzolans contain an amorphous, siliceous /aluminous fraction which reacts with lime to form cementitious hydrates similar to those found upon hydraulic lime and Portland cement hydration. Lime hardens slowly by carbonation, however pozzolans accelerate hardening and increase ultimate strength by imparting a hydraulic set. A pozzolan's activity refers to its capacity of binding lime and the rate at which the binding takes place. The reactivity of a pozzolan depends on its chemical and mineralogical composition, the type and proportion of its active phases, the particle's specific surface area, the ratio of lime to pozzolan, water content, curing time and temperature [1]. In addition, the rate of lime combination increases in the presence of sulfates such as gypsum, Na_2SO_4 and $CaCl_2$ [2]. Walker and Pavía (2011) [3] state that a pozzolan's reactivity is mainly determined by its amorphousness which in turn governs the strength of a lime: pozzolan paste. The authors established a clear relationship between increasing amorphousness and increasing strength for nine pozzolans.

This paper studies the properties and reactivity of six incinerator bottom ashes (IBAs) from several countries in Europe in order to evaluate their potential as pozzolanic additions. Partially replacing lime with ash would recycle waste and lower the CO_2 emissions and raw material consumption associated to binder production, making materials more sustainable.

Waste incineration is one of the most effective methods for the management of municipal solid waste regarding mass and volume reduction. The input waste is burned losing around 70% of its original mass and 90% of its volume, lessening the need for landfills. The incineration process involves incineration; energy recovery and air pollution control. The solid waste is fed into the furnace for incineration and, to increase the burnout, exposed to high temperature and turbulence. The average incineration temperature is at least 850 ℃, with a residence time of more than 2 seconds [4]. The residue after burning, is mostly IBA (80-90%) which usually includes silica (likely over 50% by mass), alumina, calcium carbonate and lime [5, 6].

Several authors have considered the use of bottom ash from municipal solid waste incineration in building materials [4, 7-11]. Filipponi et al. (2003) [4] claim a low chemical reactivity for bottom ash and the need to enhance reactivity. In contrast, Lin et al. (2008) [8] state that incinerator bottom ash slag is active when combined with PC and identified $Ca(OH)_2$, CSH (tobermorite) and CAH (calcium aluminate hydrate) as the main hydration products in incinerator bottom ash slag- PC pastes. Jurič et al. (2006) [12] studied the properties of bottom ash concrete concluding on a satisfactory quality for low strength requirements and the feasibility of IBA use in PC concrete.

This paper evaluates the activity of IBAs by measuring properties that determine reactivity including particle size, specific surface area, composition, microstructure, rate of lime combination in solution, strength development and ultimate strength of pastes made with ash and hydrated lime.

2 MATERIALS AND METHODS

A hydrated lime (CL90s) complying with EN 459-1 [13] and a siliceous sand with similar grading and composition to the European CEN standard sand were used. The ashes were sourced from four incineration plants. They presented a wide variation in particle size and a distinctly coarse fraction. They were oven dried at 105 ℃ to constant weight and the coarse fraction (1-2.8 mm) removed to be studied separately. Particle size reduction was carried out by ball milling using a TEMA disc mill. Homogenisation was ensured by quartering with a rotary cone sample divider to ensure representativity when small quantities were required for analyses. Table 1 includes some characteristics of the ashes.

Table 1. Combustion time and temperature at production plant of the incinerator bottom ashes studied.

Ash notation	Grading	Temperature (°C)	Residence time (min)
IBA 1	≤ 1 mm	1010	40
IBA 1/2	1- 2.8 mm	1010	40
IBA 2	≤ 1 mm	1100	unknown
IBA 2/2	1- 2.8 mm	1100	unknown
IBA 3	≤ 1 mm	950	20
IBA 3/2	1- 2.8 mm	950	20

2.1 Grading, specific surface area and microstructure of the ashes.

Grading, specific surface area and microstructure of the ashes.

The particle size distribution was measured by laser diffraction using a Mastersizer 2000 and the specific surface area determined with a Quantachrome Nova 4200e and the BET method, a model isotherm based on adsorption of gas on a surface. The mineralogical composition and amorphous character of the pozzolans was analysed by

X-Ray Diffraction (XRD), using a Phillips PW1720 XRD with a PW1050/80 goniometer and a PW3313/20 Cu k-alpha anode tube at 40kV and 20mA. All measurements were taken from 3 to 60 degrees (2θ) at a step size of 0.02 degrees/second. The microstructure and morphology of the ashes were studied with a scanning electron microscope (SEM) using Mira Tescan equipment.

2.2 Reactivity of ash by electrical conductivity

The conductivity variation of a lime-ash suspension over time was measured in order to assess the ability of the ash to combine lime - $Ca(OH)_2$ – and thus its reactivity. 0.8 g of ash were added to a saturated hydrated-lime solution (0.2 g of lime in 100 mL of water). The solution was kept at constant temperature (20ºC) and the conductivity measured at intervals over 168 hours.

2.3 Reactivity of ash by strength development

The compressive and flexural strengths of 40x40x160 mm prisms were measured according to EN 459-2 [14] and EN 196-1 [15] and compared with a standard lime mix over 90 days. The specimens were demolded after three days and cured for 90 days in a curing chamber at 20°C and 60% relative humidity.

To ensure consistency, given the wide range of particle sizes and the difference in particle size distribution between the different ashes, the water content was calculated according to the function established by Walker and Pavía [3] which sets a relationship between specific surface area and water demand, based on experimental work with 9 pozzolans. According to this, 1:1:3:1.5 (lime:ash:sand:water) was the ratio by mass for the IBAs with surface area over 7 m^2/g whereas lower surface areas (c.1-4) required less water 1:1:3:1.

3 RESULTS AND DISCUSSION

3.1 Composition, microstructure and physical properties of the ashes

Physical properties such as particle size and specific surface area determine the combination rate of lime by a pozzolan and therefore its reactivity. The particle size distribution for the ashes appears in figure 1.

According to the particle size distribution results (Figure 1), the IBAs present a wide range of particle sizes. IBA 1 and 2 contain more fines than IBA 3 whose particle size distribution compares well with lime. The meridians of the fine bottom ashes (d(0.5)=14.26, 18.28 and 16.53 µm) are lower than lime, meaning that half of the particles of the fine ashes are smaller than lime particles while the coarser ashes are comparable, except for IBA3/2 which is coarser (56.43 vs 24.13 µm for lime). The coarser IBA fractions include particles with irregular shapes and agglomerates of spherical particles agreeing with former authors [16-20].
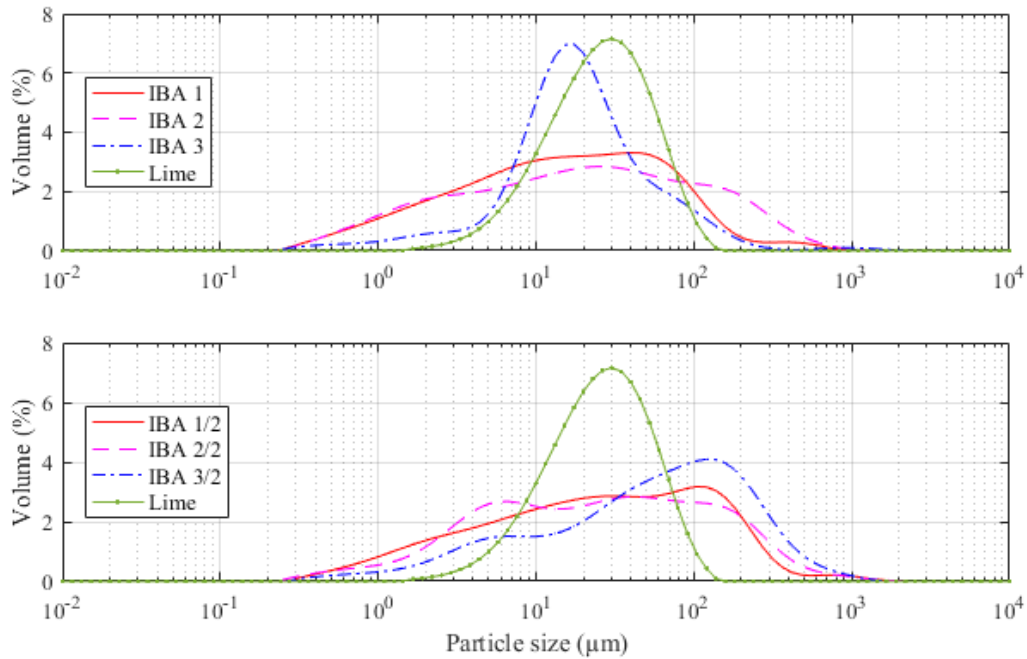
Figure 1. Particle size distribution by laser diffraction.

The specific surface area of the finer ashes is superior, ranging between 7.42 and 9.68 (m^2/g) while the coarser ashes vary between 4.47 and 6.16 (m^2/g) and the lime reached 16.09 (m^2/g) - Table 2. The values are greater than those typical of supplementary cementing materials such as GGBS and PFA, however, lower than RHA or MS [3].

XRD revealed that all incinerator ashes are intermediate to highly amorphous and consist of calcite, silica and magnetite (Table 2). Lower amounts of hematite, gehlenite and anhydrite were occasionally found.

Table 2 Mineralogical composition, amorphousness and specific surface area (lime 16.09 m^2/g).

Ash	Mineralogical composition	% Amorphousness	Surface area (m^2/g)
IBA 1	Calcite, quartz, hematite, anhydrite, magnetite	54.9	9.036
IBA 2	Calcite, quartz, magnetite	50.1	9.677
IBA 3	Calcite, quartz, gehlenite	55.5	7.422
IBA 1/2	Calcite, quartz, magnetite	54.2	6.158
IBA 2/2	Calcite, quartz	59.1	4.474
IBA 3/2	Calcite, quartz	51.2	5.474

The uneven particle size distribution determined by laser grading was also evidenced with the SEM. Under the SEM, the bottom ashes are composed of a heterogeneous mixture of particles of diverse, irregular shapes. They also include agglomerates of spherical particles agreeing with former authors [3, 16-19]. At high magnifications, it was noted that large particles are covered with fine, 'cauliflower-like' agglomerates which increase surface area and buildup porosity in the ashes (Figure 2).

SEM HV: 15.00 kV   WD: 21.65 mm   MIRA\\ TESCAN
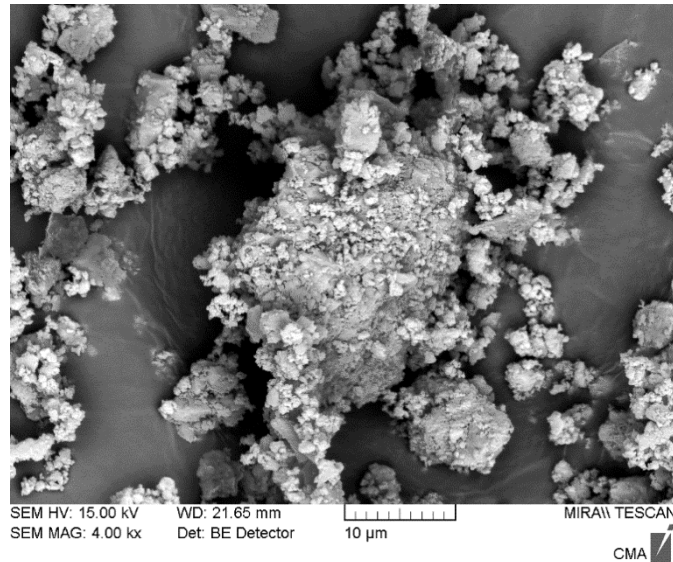SEM MAG: 4.00 kx   Det: BE Detector   10 μm   CMA

Figure 2. SEM micrograph showing the diverse, irregular shapes and sizes of the ash (IBA1) with fine, 'cauliflower-like' agglomerates increasing surface area and building up porosity in the coarse particles.

3.2 Reactivity of the ashes

The chemical test evidenced that the conductivity of all suspensions gradually lowered over time (Figure 3) therefore, the ashes combine lime and thus are reactive. As expected, the conductivity of the coarser fractions was greater than the corresponding finer fraction.

The loss of electrical conductivity of the IBA 2 suspensions is notably superior, suggesting a larger ability to combine lime therefore the greatest activity. The other ashes require at least 168 hours to cause comparable reductions in conductivity to those caused by the IBA 2 ashes in the first 24 hours. Therefore, according to the conductivity test, the IBA 2 ashes are the most reactive, followed by IBA 1 and finally IBA 3 being the least reactive.

The conductivity loss-over time curves (Figure 3) clearly show four phases agreeing with previous authors [21, 22]. During the first 24 hours (Phase I) the curves show steep slopes whereby all solutions lost over 12% of their conductivity suggesting that the ashes combine lime at a faster rate. By the end of phase I, the fine and coarse IBA3 ashes show the same conductivity while the other fines and their respective coarser fractions are well parted. Between 24 and 48 hours (Phase II) the lesser steep curves indicate a drop in the reaction rate. The percentage of conductivity loss in this phase ranges from 0.31% (IBA 3) up to 3.16% (IBA 2/2). Phase III -between 48 and 96 hours- presents a significant reduction in chemical activity (conductivity drop less than 1.5%), even a dormant period (in the case of ashes IBA2/2 and IBA 3 and 3/2) where the curves are flat. The last phase (IV) shows a new increase on the reaction rate, evidenced by the steeper slopes in the curves after 96 hours.
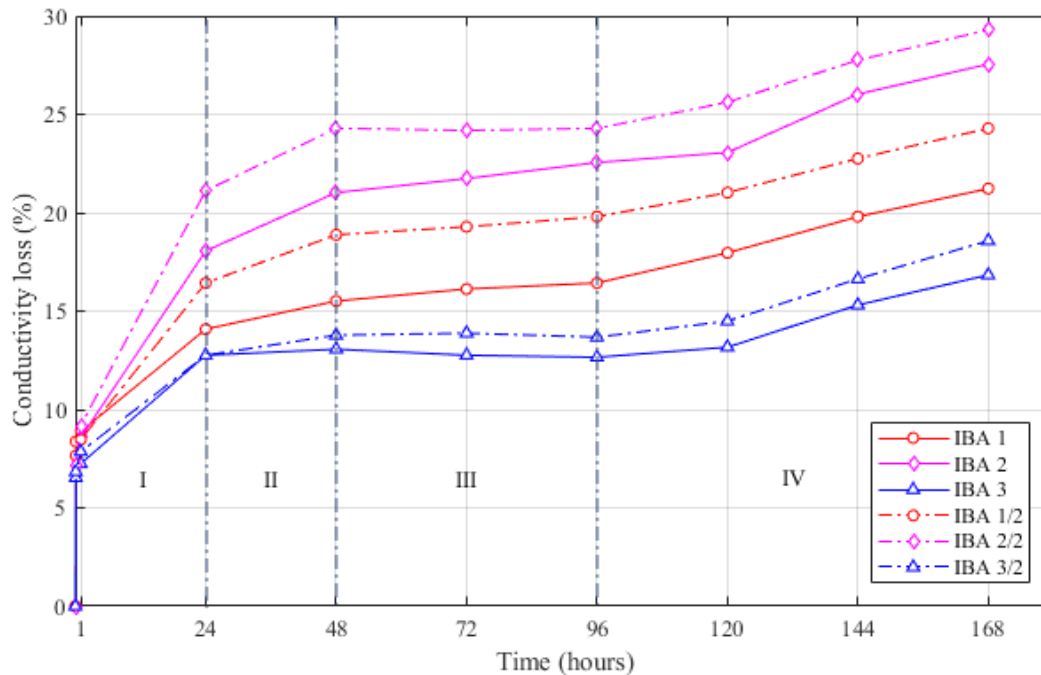
Figure 1. Electrical conductivity of ash-lime suspensions - loss in conductivity over a period of 7 days for the fine and coarser ashes.

The mechanical tests evidenced that the IBA2 specimens achieved the highest compressive strength (up to 1.67 N/mm^2) followed by the IBA1 (1.10 N/mm^2). The IBA3 specimens reached the lowest compressive strength (1,05 N/mm^2) however the highest flexural strength (0.57 N/mm^2) while the IBA 2 ash specimens, with the greatest compressive strength displayed the lowest flexural strength (0.27 N/mm^2). At 28 days, all the ash-lime mixes show a superior compressive strength than the lime alone (0.41 N/mm^2), in particular, the IBA2 and IBA1 ashes have increased the compressive strength of the lime by 4 times and over 2.5 times respectively.

3.3 Discussion

The reactivity of the ashes, evaluated with the compressive strength and the chemical conductivity tests agree, placing the ashes in the following order with decreasing reactivity: IBA 2, IBA 1 and finally IBA 3 with the lowest activity.

All the ashes significantly increased the strength of the lime alone (at least over 2.5 times), achieving strength values comparable to those produced by feebly natural hydraulic limes (NHL 2) in equivalent mixes [23].

The loss of electrical conductivity of the IBA 2 ash suggest a significantly superior initial activity for this ash. Walker and Pavía (2011) [3] state that amorphousness is the dominant factor that determines initial activity of a pozzolan. The initial activity (during the first 24 hours) of the IBAs was graded using the slopes of the conductivity loss curves of Phase I in figure 3. Table 3 compares initial activity with the amorphousness and specific surface areas previously calculated. The coarser fraction of the IBA2 ash shows the greatest conductivity loss and also the greatest amorphousness agreeing with Walker and Pavía (2011) [3], however, the second and subsequently more active ashes (IBA2 and IBA1/2) do not follow the same trend, this is probably due to the close amorphousness of all the ashes.

Table 3. Initial activity determined with the slope of the conductivity loss curve in the first 24 hours compared with the amorphousness and the specific surface area of the ashes.

Ash	Initial activity of ash (slope of conductivity loss curve in phase I)	% Amorphousness	Specific surface area (m^2/g)
IBA 1	0,59	54.9	9.04
IBA 2	0,75	50.1	9.68
IBA 3	0,53	55.5	7.42
IBA 1/2	0,68	54.2	6.16
IBA 2/2	**0,88**	**59.1**	4.48
IBA 3/2	0,53	51.2	5.48

The fineness of the ashes, with half of the particles of the finer ashes smaller than lime particles, as well as their high specific surface area and amorphousness, are consistent with their activity. The mineral composition and the presence of high temperature oxides are consistent with their production technology and composition reported by former authors. Traces of anhydrite were occasionally found in one ash only, lessening the possibility of sulfate attack.

A positive correlation was found between specific surface area and compressive strength ($p - value = 0.016$), indicating that the results are statistically significant to reject the null hypothesis (H_0), therefore, the hypothesis that compressive strength increases proportionally to the surface area may be supported - Figure 2. However the flexural strength shows the opposite trend ($p - value = 0.006$). This value is also smaller than the significance level of 5% ($\propto = 0.05$), and it is known that the smaller the p-value, the heavier the weight of the sample evidence for rejecting H_0, i.e. at a significance level of .05 the hypothesis that there is no correlation between surface area and the studied strengths (null hypothesis) can be rejected.

The Pearson correlation also supports the existence of these relationships. It examines the strength and direction of the linear relationship between the studied properties. The correlation ranges between +1 and −1, where 1 is total positive linear correlation, −1 means total negative linear correlation and 0 indicates that there is no association between the two variables. It is acknowledged that values greater than 0.7 or smaller than –0.7 describe a strong strength of association.
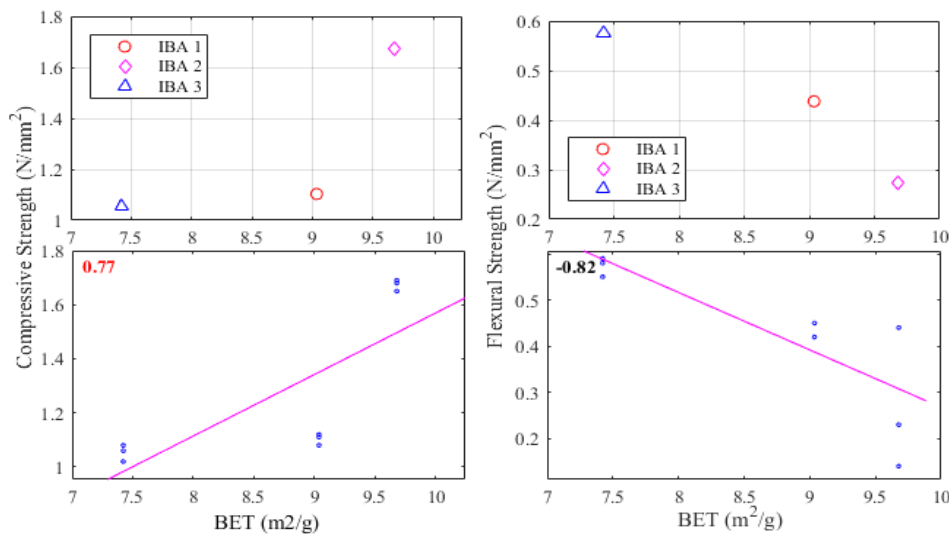

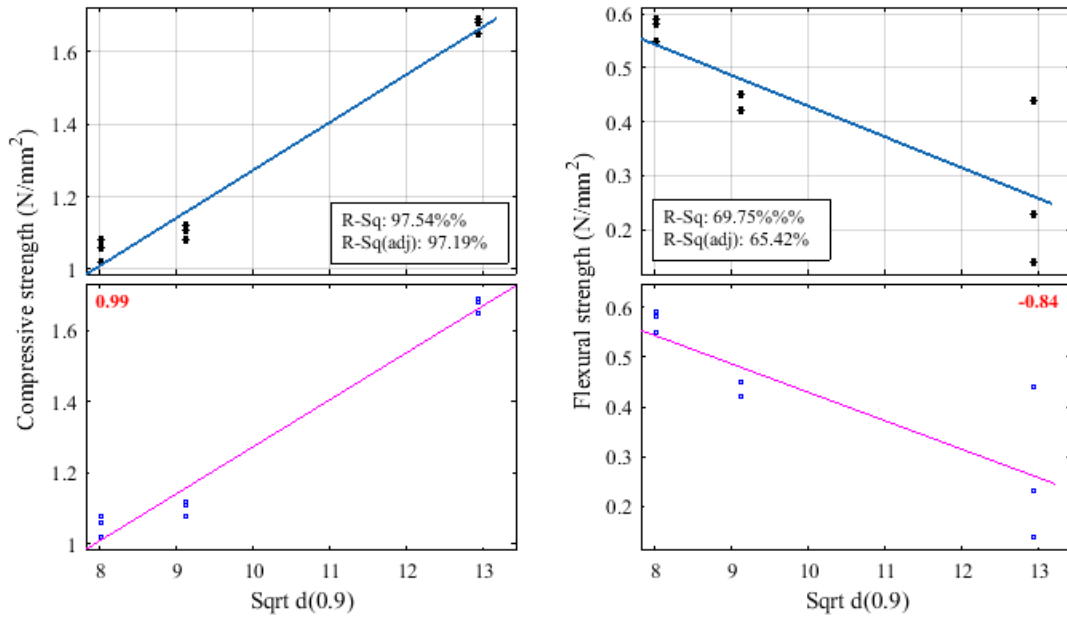Figure 2. Relationship between specific surface area and compressive and flexural strengths

Figure 5 Relationship between particle size and compressive and flexural strengths

It was also evidenced that the particle size of the ashes shows an inverse relationship with flexural strength (Figure 5) which lowers as the particle size increases. In contrast, the compressive strength increases with the ash particle size in the range 64.23 µm – 167.31 µm (corresponding to 8.01 to 12.93 Sqrt d(0.9) - Figure 5). A Pearson correlation coefficient equal to 0.99 confirms a good relationship.
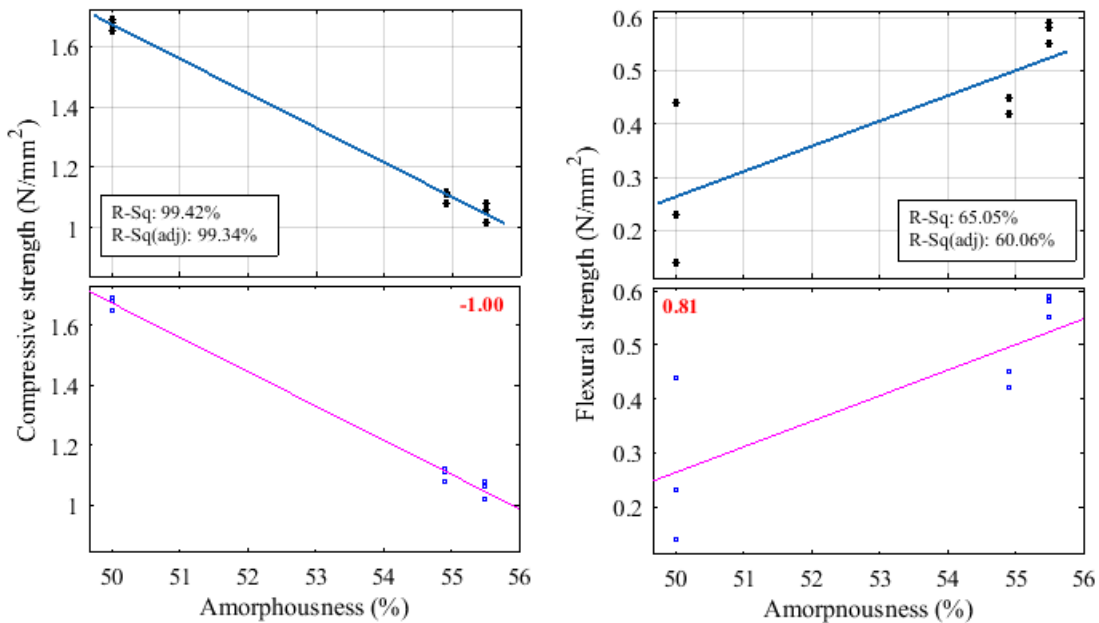

Figure 6 Relationship between amorphousness and compressive and flexural strengths

Regression analysis indicates that the amorphousness of the ashes relates well to the compressive strength development (compressive strength vs amorphous content fit well with a polynomial curve ($R^2 = 0.99$)- Figure 6.

It can also be seen from Figure 6 that flexural strength shows a positive linear relationship with amorphousness. Flexural strength only shows a positive linear

relationship with amorphousness (inverse relationships were established with particle size and surface area- Figures 4 and 5) this can indicate that the development of the flexural strength is more sensitive to amorphousness, thus chemical characteristics (chemical bonds that are more likely to occur with amorphous phases) whereas compressive strength is rather governed by physical properties such as particle size and surface area.

4 CONCLUSION

Both the electrical conductivity test and the strength development evidenced reactivity for the ashes. All the ashes significantly increased the strength of hydrated lime alone between 2.5 and over 4 times, achieving strength values comparable to those of feebly hydraulic limes in equivalent mixes.

Both the electrical conductivity test and the strength development place the ashes in the same order of decreasing reactivity: IBA 2, IBA 1 and finally IBA 3 with the lowest activity.

The fineness of the ashes, with half of the particles of the finer ashes smaller than lime particles, as well as their high specific surface area and amorphousness, are consistent with their activity. Traces of anhydrite were occasionally found in one ash only, lessening the possibility of sulfate attack.

Flexural strength shows a positive linear relationship with amorphousness however inverse relationships with particle size and surface area suggesting that flexural strength development is more sensitive to amorphousness, thus chemical characteristics (chemical bonds that are more likely to occur with amorphous phases) while compressive strength (which shows a positive correlation with specific surface area/ particle size) is rather governed by physical properties.

5 ACKNOWLEDGEMENTS

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