EFFECT OF POZZOLAN PROPERTIES ON THE PROPERTIES OF BUILDING COMPOSITES

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Abstract

Pozzolans were used by ancient civilizations to enhance the properties of mortars and concrete and are now regaining popularity as sustainable, environmentally-friendly alternatives to cement. This paper studies the relationships amongst some properties of nine pozzolans and their impact on compressive strength and setting time of the resultant composites. Its objective is to assist in making informed choices in the selection of pozzolans for the production of mortars and concrete. Results indicate that each pozzolan has a specific water demand that increases with its specific surface area; and that a high water demand by the pozzolan slows down the setting of the paste but does not undermine the strength of the composite. It was also found that specific surface has a much greater influence on the water demand of the paste than particle size or lime:pozzolan ratio. The results exposed the adverse effect of a small water increase on setting time, and the lack of relationship between setting and reactivity. It was evidenced that the pozzolans accelerate the final set of lime by at least 40%, and that the specific surface area of the pozzolan and its amorphousness are the most important variables affecting reactivity and strength. Strength development and reactivity results allowed determining the most reactive pozzolans.

Keywords: pozzolan, particle size, specific surface, amorphousness, water demand, reactivity, compressive strength, setting time

1. Introduction

Pozzolans are materials with an amorphous siliceous or siliceous and aluminous content that react with portlandite ($Ca(OH)_2$) in the presence of water to form cementitious hydration products (calcium silicate and calcium silicate aluminate hydrates). They have been used to enhance the properties of composites since antiquity. The oldest evidence of the use of pozzolans has been found in the Neolithic period (7000 BC) in Galilee (Caijun 2001 refering to Malinowski et al.). Today, growing environmental concerns have focused on reusing and recycling materials. Pozzolans are often industrial or agricultural by-products. Using them in composites carries environmental benefits, reducing the negative environmental impact of building. The replacement of conventional industrial binders by pozzolanic waste material lowers the cost of construction and enables, not only recycling waste whose disposal poses a threat for the environment, but also reducing energy consumption, non-renewable, raw material consumption and CO_2 emissions (Pavía & Regan 2010).

Pozzolans can enhance durability of composites so they are used in the production of high performance PC concrete with a view to improve the service life of concrete structures. The filler effect of pozzolans increasing density and strength is well known and has been previously reported. When used as additions in lime or PC composites,

pozzolans can act as nuclei for the precipitation of hydration products refining pore structures and increasing density plus reducing porosity on account of their filler effect. In contrast, pozzolans partially replacing PC usually result in materials of higher porosity (especially at early ages due to a reduction of hydration products) but lower permeability and sorptivity and smaller diffusion coefficients than the parent PC (Massazza refering to Day et al. 1989; Ganesan et al. 2008; Chindaprasirt and Rukzon 2009). As a result, the penetration of ions, both by capillary suction and by diffusion, is lower in pozzolan cements than in PC pastes and, therefore, their resistance to salt attack and leaching of lime improves (O'Donnell et al. 1995; Higgins 2003; Luo et al. 2003; Chindaprasirt et al. 2007). The resistance of pozzolan cements to sulfate attack is further increased as replacement of PC by pozzolan lowers C_3A and $Ca(OH)_2$ content (Massazza 2007). In addition, pozzolans enhance mechanical properties of PC composites (Al-Jabri et al. 2006; Shoaib et al. 2000; Giacio et al. 2007). They also affect the kinetics of hydration, the composition of some hydrates and the heat of hydration of PC composites (replacing PC by pozzolan decreases the initial autogenous temperature rise of PC - Sánchez de Rojas & Frías 1996; Mostafaa & Brown 2005). Some pozzolans reduce the alkalinity of the pore solution, and this impacts the durability of concrete.

This paper studies the impact of some physical properties of pozzolans including particle size, specific surface, amorphousness, water demand and reactivity, on the density, porosity, compressive strength and setting time of composites, in order to understand and predict the behavior and quality of pozzolan composites for building. Lime pastes were used however, the results are applicable to both PC and lime composites as, in both cases, pozzolanic reaction is based on portlandite consumption.

When mixed with PC and water, pozzolans react with the portlandite formed during hydration of calcium silicates. As a result, the portlandite content pozzolan-PC pastes is lower than that of the parent PC. This results in a reduction in the number and size of portlandite crystals both in the paste and at the aggregate interface which improves the microstructure of the paste by decreasing flaws, enhancing the homogeneity of the matrix (Massazza 2007), and reinforcing the microstructure of the transition zone (Massazza refering to Bentur at al. 1987; Zhang et al. 1996). In general, replacement of PC by pozzolans lowers early strength and improves the long term one: initially, the pozzolan behaves as an inert material reducing the initial rate of strength gain. However, at greater ages, pozzolanic reaction begins and pozzolan cements attain the same or higher strengths than the parent PC.

When mixed with lime and water, pozzolans react with portlandite forming hydration cements similar to those found upon hydration of PC and hydraulic limes. Pozzolans accelerate the slow hardening process (carbonation) of calcium limes by imparting a hydraulic set. Pozzolanic reaction is slow, thus early strength does not increase, however, when combined in the right ratio, pozzolans increase the ultimate strength of lime composites: the compressive strength at 2 years can be as high as 3 times the 28-day strength (Massaza 2007).

Particle size, specific surface and amorphousness have been linked to reactivity by former authors. It is widely accepted that an increase of specific area and/or decrease in particle size will expose a greater surface to chemical reaction enhancing reactivity, and that amorphous structures are more reactive than crystalline ones on account of the greater mobility and superficial location of their atoms: glassy pozzolans are considered to be active, while weak pozzolans have a low glass content associated to significant amounts of crystalline minerals. There is also an obvious relationship

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between pozzolan reactivity and compressive strength of the resultant composite (the hydration products of the pozzolanic reaction contribute to the strength of the paste).

The setting time of some pozzolan cement does not differ from that of PC. Some pozzolans such as fly ash usually delay both initial and final setting times (Massazza 2007 refering to Berry and Malhotra 1987). Finally, pozzolans can either increase or reduce water demand, depending on the nature of the pozzolan and the properties of the binder with which they are mixed.

2. Materials and Methods

2.1 Materials
Nine pozzolans were studied including Ground Granulated Blastfurnace Slag (GGBS); Leca; Pulverised Fuel Ash (PFA); Calcined Clay (MetaStar); Microsilica (MS); Rice Husk Ash (RHA); Red Brick Dust (RBD); Tile and Yellow Brick Dust (YBD). Two lime:pozzolan ratios 1:1 and 1:3 (by weight) were investigated. The water content was fixed to produce a flow diameter of 165mm. A hydrated commercial lime (CL90s) complying with EN 459-1was used.

2.2 Properties of the pozzolans
Chemical composition was determined by XRF analysis, using a Quant'X EDX Spectrometer and a UniQuant analysis package. The samples were mixed with Hoescht wax and pressed into aluminum cups using a 10 tonne hydraulic press. Amorphoussness was analysed by X-Ray Diffraction (XRD) using a PW1720 XRD with a PW1050/80 goniometer and a PW3313/20 Cu k-alpha anode tube at 40kV and 20mA. Measurements were taken from 3 to 60 degrees (2θ) at 0.02 degrees/second. Particle size was determined with laser diffraction (Malvern Mastersizer 2000). Specific surface area was measured using a Quantachrome Nova 4200e and the BET method, a model isotherm based on adsorption of gas on a surface.

2.3 Reactivity of pozzolans: chemical activity index
This method follows the pozzolanic reaction indirectly by measuring the changes in the conductivity of a saturated lime and pozzolan solution. The fixation of dissolved $Ca(OH)_2$ reduces portlandite concentration in solution, leading to a decrease in conductivity. 4g of pozzolan were added into a saturated solution of lime (electrical conductivity reading 9.8mS at 20°C). The solution was continuously stirred by a magnetic stirrer and the conductivity and temperature measured at intervals over 125hours using a WTW LF 197 conductivity meter with a Tetracon 325 probe.

2.4 Pozzolan water demand and setting time of the paste
Water demand was assessed by measuring initial flow in accordance with EN459 for ratios 1:1 and 1:3 (lime:pozzolan). The water content was adjusted to produce a 165mm flow diameter. Mixing was in accordance with EN 459 except for the addition of the pozzolan (added after 1 minute and the mixing stopped for 30 seconds). Setting times were measured on the pastes above, including the water required in order to produce a standard consistency (165mm flow).

2.5 Compressive strength development
The prisms were demoulded after 1 day and stored in a curing room at 20°C±3°C temperature under damp hessian to maintain humidity at c.95%. The unconfined

compressive test was measured with a Zwick loading machine according to EN459. Water content was determined by fixing initial flow: the low water demand pozzolans (GGBS, Leca, PFA, RBD, Tile and YBD) were given a lime:pozzolan:sand:water ratio of 1:1:3:1 and therefore a binder: water ratio of 0.5 while the ratio for those with a with a higher water demand (Meta, MS and RHA) was 1:1:3:1.5.

2.6 Bulk/real densities and porosity
These were tested on the compressive strength samples (RILEM 1980). Bulk density (δ) is the ratio of the dry mass of the sample to its bulk volume while real density (δr) is the ratio of the dry mass to its impermeable volume. Both inform on grain packing and compaction and enable calculating the effective or open porosity (P).

3. Results

3.1 Particle size, surface area, composition, amorphousness and water demand.
Figure 1 includes the particle size distribution of the pozzolans. According to the results, Metastar, RHA and GGBS are the finest. The microsilica particles flocculated during the laser analysis on account of their extremely small size, therefore, the MS is finer than determined by the laser method. According to the specific surface area results (Table 1), MS, Metastar and RHA have a much greater specific surface than any of the other pozzolans.
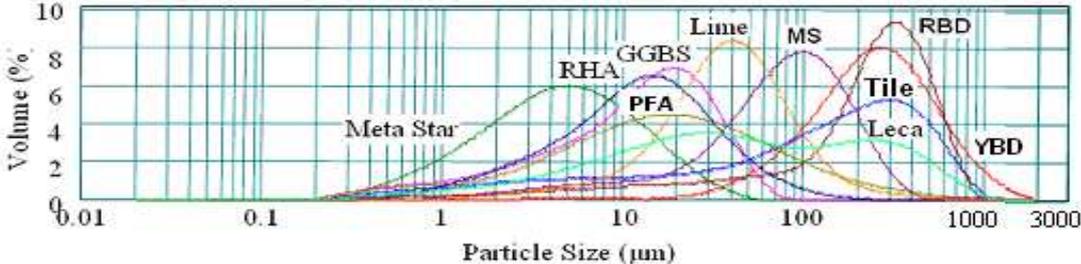
Figure 1 - Particle size distribution of pozzolans.

Table 1 - Specific surface area of pozzolans.

Pozzolan	GGBS	Leca	PFA	Meta	MS	RBD	RHA	Tile	YBD
Surface area m²/g	2.65	1.28	4.09	18.3	23.6	4.29	13.7	4.16	0.31

The chemical composition and amorphousness of the pozzolans are included in table 2. Amorphousness was loosely categorised into 4 groups ranging from totally amorphous (displaying a large amorphous hump and no crystalline fraction in the XRD pattern) to slightly amorphous (very small amorphous hump). According to these, GGBS, Meta, MS and RHA are the most reactive; followed by Leca and PFA. Finally, YBD, RBD and Tile are the least active pozzolans. The water demand of each pozzolan was calculated based on the water demand of the lime (water:lime ratio for the lime to flow 165mm is 0.862), the amount of lime and pozzolan, and the total water content of the paste. According to the results, the pozzolans were divided into two groups of high (Meta, MS and RHA) and low (GGBS, Leca, PFA, RBD, Tile and YBD) water demand respectively.

Table 2 - Chemical composition and amorphousness of the pozzolans. – not detected.

Pozzolan	SiO$_2$	Al$_2$O$_3$	CaO	Fe$_2$O$_3$	SO$_3$	MnO	K$_2$O	MgO	Rate of amorphousness
GGBS	34.14	13.85	39.27	0.41	2.43	0.25	0.26	8.63	(5) Totally
Leca	52.78	24.39	3.59	11.42	0.39	0.37	2.82	2.70	(3) Intermediate
Meta	51.37	45.26	-	0.52	-	-	2.13	0.55	(4) Mostly
MS	92.10	2.13	1.10	1.62	0.28	-	1.32	1.05	(4) Mostly
PFA	65.32	24.72	0.94	4.84	0.37	-	1.37	0.68	(3-2) Intermediate to slightly
RBD	48.24	22.15	10.31	6.67	6.94	-	2.97	1.17	(2) Slightly
RHA	93.84	1.93	0.68	0.29	-	0.12	1.38	0.45	(4) Mostly
Tile	46.61	21.47	11.34	7.19	7.62	-	3.05	1.12	(2) Slightly
YBD	43.90	44.94	0.36	2.11	-	-	1.27	6.28	(2) Slightly

3.2 Effect of pozzolan properties on water demand

The results indicate that water demand depends on the pozzolan's particle size and specific surface, and on the lime:pozzolan ratio (Figure 2). However, specific surface has a considerably greater influence on water demand than particle size or ratio. As expected, the greater surface pozzolans had a higher water demand. Specific surface has a much greater influence on water demand than particle size (RHA and GGBS have a similar particle size but RHA has a greater surface and significantly higher water demand). It was noted that replacing lime by pozzolan lowered the water demand of all pastes with the exception of Metastar. This is due to the greater water demand of the Metastar with respect to lime on account of its high specific surface.
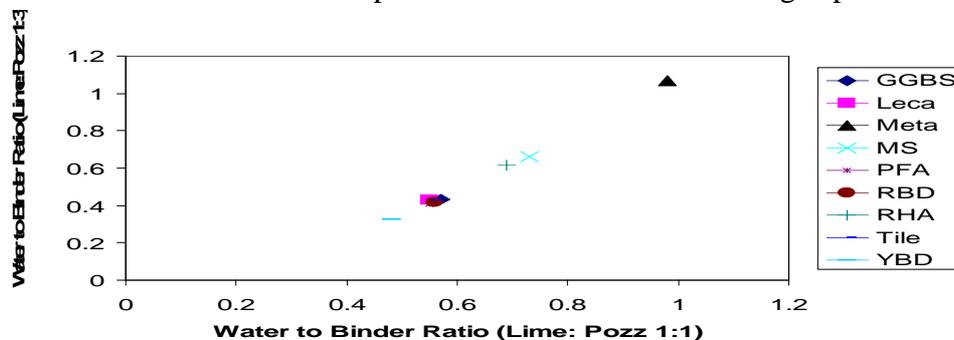
Figure 2 - Water demand of pozzolans in lime:pozzolan pastes of ratios 1:3 and 1:1

3.3 Reactivity of pozzolans and strength development of the paste

A high reactivity (acceleration of the pozzolanic reaction) positively affects strength development because strength builds up with increasing amount of combined lime. Therefore, strength development and reactivity (chemical index) are closely related.

According to the strength and chemical index results (Table 3), Metastar, GGBS, RHA and MS are the most reactive (Walker and Pavía 2010). These pozzolans are either totally (GGBS) or mostly amorphous (Metastar, RHA and MS). In addition, Metastar, RHA and MS have a specific surface much higher than any of the other pozzolans, while GGBS has a lower specific surface but it is amongst the finest. This indicates that specific surface and amorphousness are important variables affecting reactivity and strength development. Although not sensitive to the chemical reactivity

index, GGBS has a strength comparable to that of Metastar, much higher than any of the other pozzolans, therefore, it can be considered amongst the most reactive.

Table 3. Pozzolan reactivity and compressive strength of the paste. (*) ratio of the compressive strength of the lime/pozzolan mix to a standard lime/sand mix.

Pozzolan	Compressive strength (*)	Chemical Activity Index	
		Phase 1 % drop	Latent Period (hrs)
GGBS	29.5	-	-
Leca	4.6	-	-
PFA	3.4	3.4	65.0
Meta	38.1	9.8	18.0
MS	12.5	4.3	39.5
RBD	2.5	2.5	91
RHA	12.0	6.8	55.0
Tile	3.3	3.5	90.0
YBD	1.2	3.9	67.0

Strength increases with decreasing particle size (Figure 3). The well known filler effect of fine pozzolans is partially responsible for the high strength of the finer pozzolans (GGBS, Metastar and RHA). A clear relationship between increasing amorphoussness (Table 3) and increasing reactivity was established for the nine pozzolans (Figure 4). In addition, the higher water demand pozzolans show the greatest 28-day strength, therefore, water demand of the pozzolan does not affect compressive strength of the paste. Metastar and GGBS higher compressive strength values than any other pozzolan; followed by the high-silica RHA and MS (68% reduction); and finally the PFA, Leca and brick dusts (89% lower than the Metastar).
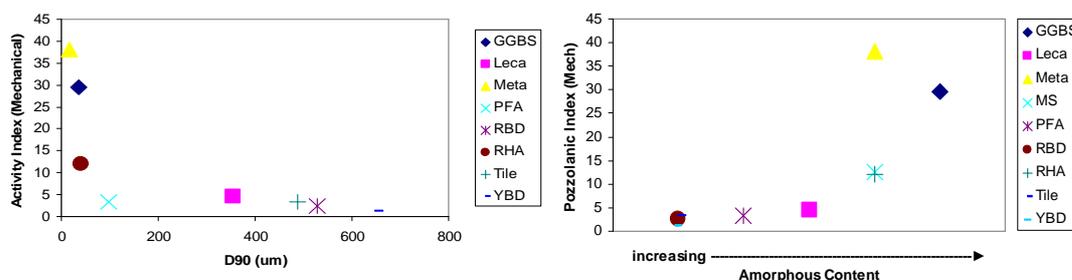
Figure 3&4- Relationship between particle size and strength development (left) and influence of increasing pozzolan amorphousness on strength (right)

3.4 Setting time

All pozzolans reduced the final setting time (when compared to that of the lime alone) by at least 40% (Figure 5). In addition, except for PFA and MS, the pozzolans also accelerated the initial set (Figure 5). The results did not evidence a relationship between setting time and pozzolan reactivity, this may be due to the low speed of the pozzolanic reaction. In addition, a pozzolan can be more reactive than other and yet need more time to set if the hydration products initially formed make a smaller contribution to the stiffness of the paste.

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It was evidenced that a small increase in water content (5%) significantly retards setting. The adverse influence of water increase was also evidenced in the Metastar paste. Here, due to the great water requirement of this pozzolan, setting time had to be measured in a 1:3 paste which provided values comparable to those of other pozzolans in 1:1 pastes. It can be seen from the results that the GGBS paste sets significantly faster than any other paste. It is the fastest to develop an initial set and takes only 7 hours to fully set. GGBS can contain calcium silicates and aluminates similar to those found in PC clinkers, thus being a hydraulic rather than a pozzolanic material. Neither silicates nor aluminates were detected with XRD in the GGBS, however, it can contain a small amount of silicates/aluminates that are accelerating set (the limit of detection is 5%). In addition, the GGBS contains little alumina (13.85%), however, it is the only pozzolan that is totally amorphous and has a high calcium content (39.27%). These may also contribute to the early set of the GGBS paste.
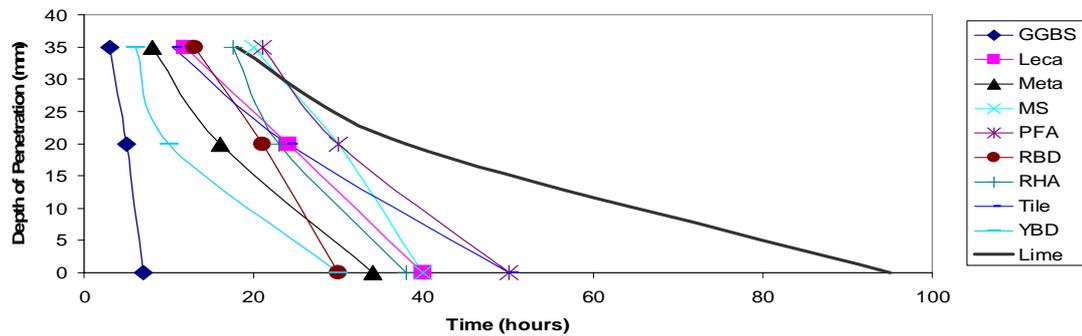
Figure 5. Setting time of lime and lime:pozzolan pastes at ratio 1:3, except for Metastar with a ratio of 1:1 (each value is an average of 3 results).

3.5 Densities and porosity

The high water demand pozzolans (Meta, RHA and MS) display the lowest real density and greatest difference between real and bulk density thus including the greatest amount of voids. In contrast, the low water demand pozzolans (GGBS, PFA, RBD, Tile and YBD) have a real density greater than that of the reference lime. The results agree with Papayianni (2006) who determined that, in lime pozzolan mortars, water/binder ratio is the most important factor influencing porosity.
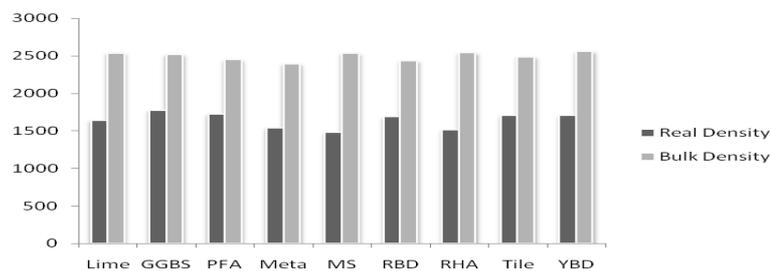
Figure 6. Real and bulk densities of lime:pozzolan mortars.

For both the high and low water demand pozzolans, a relationship between particle size and porosity was evident (figure 7), with porosity reducing as pozzolan particle size decreases. The well established relationship between increasing strength with reducing porosity in lime pozzolan mortars was evident at the two water contents (figure 8). However as noted by Papayianni (2006), strength is also dependant on the

pozzolanic reactivity and hence the Meta, RHA and MS despite having a higher porosity on account of the high water demand also have a higher strength.
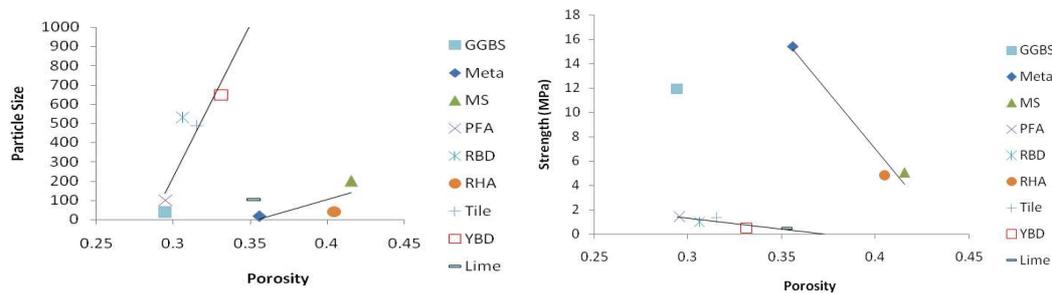
Figure 7&8 - Relationship between porosity and particle size (left) and strength (right).

4. Conclusion

The conclusions below can contribute to making an informed choice in the selection of pozzolans for the production of quality building composites.

When high reactivity and a high strength development rate are required, pozzolans of high specific surface area and amorphousness should be used. The fact that strength also increases with decreasing particle size should also be taken into account. According to the strength development and the reactivity results, Metastar, GGBS, RHA and MS are the most reactive pozzolans.

Water content should be carefully determined in the production of pozzolan composites as a small increase in water content will significantly retard the set and will increase the porosity of the composite. Each pozzolan has a specific water demand that is mainly determined by its specific surface area, however, a high water demand by the pozzolan will not undermine the composite's compressive strength.

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