Improving circular economy by the valorization of non-conventional coal fly ashes in composite cement manufacturing

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Keywords: coal fly ash; coal combustion; spreader stoker; composite cements, eco-cement

Abstract

Spreader Stoker thermal power plants are initially used to burn bagasse during the sugarcane harvest, but also coal when the season is over. The drawback is that, compared to standard pulverized coal fly ashes, the coal fly ashes resulting from this process contain many more unburned particles. Therefore, Spreader Stoker Coal Fly Ash (SSCFA) is sent to landfill despite its potential for valorisation in construction. The main objective of this work was to evaluate the potential of laboratory manufactured composite cements incorporating SSCFA by using a variety of manufacturing methods, such as co-grinding/separate grinding of the components, and grinding of laboratory cements to equivalent global fineness. The behaviour in the fresh, hardening and hardened states was investigated to bring out the influence of Blaine specific surface and type of addition in different combinations of composite cements. Despite the high carbon content of the coal fly ash studied, the mechanical behaviour of SSCFA-cements was better than that of cement with the local pozzolan, which is the reference in Reunion Island. In addition, the use of slag and the pozzolan/SSCFA association in composite cements showed good results. An artificial neural network approach was employed to predict compressive strength in mortars with parameters such as amounts of clinker, gypsum, pozzolana, SSCFA and slag, and the Blaine specific surface. The results also enabled compressive strength response curves to be developed for mixes according to the amount of clinker in the cements.

1. INTRODUCTION

Several wastes and by-products have long been used in the manufacture of composite cements. For instance, fly ash, blast furnace slag and silica fume are used all over the world in partial replacement of clinker [1]. However, the exploitation of these by-products is usually regulated by standards, as is the case in Europe with standard EN 197-1 [2]. Currently, it is not possible to employ by-products indiscriminately and permitted ones must meet specific guidelines regarding physical and chemical properties [3].

On the one hand, local situations may exist where non-standard by-products could be used, although they do not meet all the requirements. Such is the case for Reunion Island, a small French island (2512 km^2) that produces more than 30 000 tons of coal fly ash per year in its spreader stoker power plants. Despite their potential for valorization in construction having been shown in previous studies [4, 5], these ashes (referred to as SSCFA for Spreader Stoker Coal Fly Ashes) are currently sent to landfill because they do not comply with standard EN 450-1 [3] (fly ash standard) and EN 197-1 [2] (cement standard including, among others, coal fly ash conform to EN 450-1), which covers only fly ashes obtained by burning pulverized coal. SSCFA also contain a large amount of unburned carbon particles, far above that recommended in the European Standard EN 450-1 for fly ash and EN 197-1 for the use of fly ash in cements. Unburned carbon in fly ash could sometimes be detrimental to the rheology or the air entrainment of the concrete [6, 7], or even responsible of some durability properties [8, 9]. Moreover, natural radioactivity fly ash might needed to be assessed before their use for cement manufacturing [10]. Although these issues must be addressed, SSCFA-based mortar has shown interesting mechanical properties, with a strength activity index much higher than the minimum value specified in standard EN 197-1, probably due to its high pozzolanic activity.

On the other hand, Reunion Island has no cement plants. Clinker imported from other countries is ground locally and mixed with a natural pozzolana to manufacture CEM II cements. The use of fly ashes produced locally could lead to real progress in the sustainable development of the island, since their rational valorization could simultaneously decrease the amounts of clinker to be imported, of pozzolana exploited and of SSCFA sent to landfills.

This kind of by-products will probably be increasingly used in the future for the manufacture of cements, in order to reduce the carbon impact of ordinary Portland cement and improve the circular economy. Reducing clinker content is one of the ways possible to achieve carbon neutrality, as stated in several roadmaps published in the literature (see for instance [11]).

The aim of this paper is thus to illustrate how a non-conventional fly ash could be used to develop a composite cement. It investigates the reuse of SSCFA in such an application. The first part will describe the grinding methods applied to make the laboratory composite cement. Then, a brief characterization of these manufactured cements will be reported, along with the evaluation of fresh, hardening and hardened properties of cement pastes and mortars. Finally, an approach using Artificial Neural Networks (ANN) will be presented to predict the 28-day compressive strength on mortars of the composite cements manufactured in the laboratory.

2. MATERIALS AND METHODS

2.1. Materials

The high carbon coal fly ashes studied were produced in a power plant located in Reunion Island, which uses a spreader stoker type boiler. The power plant burns bagasse during the sugarcane harvest and produces ashes that are already reused in other applications. For the rest of the year, imported coal is burned instead of bagasse, producing SSCFA that are then landfilled. SSCFA have been characterized in previous studies, showing many similarities with standard pulverized coal fly ashes but also some differences, such as the amount of unburned carbon [4, 5]. This is why it can be related to high carbon coal fly ash.

Clinker, gypsum, slag and natural pozzolana used to manufacture the laboratory composite cements were the same as the local materials (constituent from commercial cements in Reunion Island, LafargeHolcim). The sand used in mortar production was normalized quartz sand conforming to EN 196-1 [12].

The chemical compositions, including the percentage of unburned particles (LOI: Loss On Ignition), and the physical characteristics of the materials selected for this study are detailed in Table 1. SSCFA have a composition approaching that of silico-aluminous fly ashes from pulverized coal thermal power plants, with 80 wt% of SiO_2 + Al_2O_3 + Fe_2O_3 when the unburned content is excluded from the calculation. This unburned content is very high compared to that of class F fly ashes [4,13,14].

Table 1: Chemical composition (wt%) and physical characteristics of materials used to manufacture composite cements

Oxide wt%	Clinker	SSCFA	Pozzolana	Slag	Gypsum
SiO_2	20.9	35.9	52.3	34.5	0.6
Al_2O_3	5.1	20.6	16.0	12.6	0.2
CaO	65.7	4.3	5.5	37.5	38.0
Fe_2O_3	3.4	3.4	11.0	0.8	0.1
K_2O	0.4		2.0	0.8	0.0
Na_2O	0.2	0.2	3.8	0.3	0.0
MgO	2.0	0.9	2.4	9.6	0.0
MnO_2	0.1		0.3	0.3	
TiO_2	0.3	1.2	2.1	0.4	0.0
P_2O_5	0.1	1.8	0.4	0.0	
F	0.0	0.0	0.0	0.9	
SO_3	0.6	0.7	0.1	0.1	53.5
LOI	1.3	31.1	4.2	2.1	7.4
Specific gravity (g/cm^3)	3.19	2.16	2.66	2.85	2.32
Blaine specific surface (cm^2/g)	3600	5500	5700	4100	6100

2.2. Methods

The chemical composition was determined by inductively coupled plasma-optical emission spectrometry (ICP–OES, Optima 7000 DV). The sample preparation used for chemical analyses was based on borate fusion. A mixture of fly ash, lithium tetraborate and lithium metaborate was placed in a muffle furnace at 1100°C for 30 min. The melt was then carefully dissolved in diluted nitric acid before ICP–OES analyses. The loss on ignition was determined at 1000 °C according to EN 196-2 [15]. Specific gravity was found by hydrostatic weighing and the Blaine method was used to determine the specific surface (EN 196-6) [16]. The laboratory cements were ground in a 1L planetary ball mill (CONTROLS model D461/C) with 90 ceramic balls around 15 mm in diameter. Consistency and setting time tests were carried out on pastes with various water to binder (W/B) ratios in order to reach the same consistency [2]. The mortars were cast in 4*4*16 cm moulds according to EN 196-1. The tests on cement pastes and mortars included normalized consistency (EN 196-3) [17], setting time (EN 196-3), flowing time on mortars (NF P 15-437) [18] and compressive strength on mortars (EN 196-1). Compressive strength was measured at 7, 28 and 90 days on 4x4x16 cm prisms (loading speed of 2 400 N/s ± 200 N/s) according to EN 196-1.

2.3. Manufacture of laboratory cements

Several options were possible for the choice of composite cements to manufacture, according to the reference table from standard EN 197-1, which shows the current cement families [2]. Table 2 gives the names and details of the composite cements manufactured for this study. In this table, the numbers represent the percentages by weight for the components concerned (these values are within the allowed range specified in EN 197-1).

The cements marketed in Reunion Island are essentially CEM II/A-P and CEM II/B-P, which are composite cements with natural pozzolana. In order to be consistent with the properties of cements on the market, it was thus essential to compare SSCFA versus pozzolana additions, but also go deeper into the research to suggest different types of composite cements based on slag, pozzolana and fly ashes. It should be noted that the reference cements CEM II/A-P and CEM II/B-P were manufactured in the laboratory in order to have the same conditions of production as the new cements made with SSCFA. As will be explained in the following parts, for the composite cement manufactured at a laboratory scale, three grinding methods were used, each having a specific objective.

Table 2: List and composition of manufactured cements

Cement designation	Clinker	Slag	Pozzolana	Fly ash (SSCFA)	Gypsum
	K (wt%)	S (wt%)	P (wt%)	V (wt%)	G (wt%)
II/A-P15	83	-	13	-	4
II/A-V15	83	-	-	13	4
II/A-V20	78	-	-	18	4
II/A-M (P5-V15)	78	-	4	14	4

II/B-V25	73	-	-	23	4
II/A-M (P5-V20)	73	-	4	19	4
II/B-P30	68	-	28	-	4
II/B-V30	68	-	-	28	4
II/B-V35	63	-	-	33	4
II/A-M (P10-V25)	63	-	9	24	4
V/A-S20-V20	58	19	-	19	4
V/A-S20-P20	58	19	19	-	4
V/A-S20-P10-V10	59	19	9	9	4
V/A-S20-P10-V20	49	19	9	19	4

2.3.1. Separate grinding

Each ingredient (clinker, pozzolana, slag, gypsum) was ground separately before the mixture was homogenized in the mill for around 1.5 min. Specific gravity and final specific surface values are specified in Table 1 for the components of manufactured composite cements. Clinker and slag were milled to a fineness considered sufficient for good reactivity, i.e. about 3500 cm²/g for clinker and about 4000 cm²/g for slag [19-21]. Note that grindability refers to the speed and ease with which the material can be ground here. In our case, slag seemed to be more grindable than clinker, with a higher specific surface for an equivalent grinding time. However, according to the literature, slag usually presents lower grindability than clinker [19]. The pozzolana was crushed to achieve a Blaine specific surface equivalent to that of SSCFA, i.e., close to 5500 cm²/g. Considering the high grindability of gypsum, its fineness was set at 6100 cm²/g after just 5 minutes of grinding. The main advantage of this kind of grinding is the possibility of controlling the initial fineness of each constituent of the cement.

2.3.2. Co-grinding

The co-grinding method consists of weighing and inserting the different constituents of the cement directly into the mill and grinding them together. A co-grinding time of 35 minutes was chosen through a preliminary test carried out on the CEM II/A-P15 reference cement that was manufactured. The objective was to determine the time required to obtain a Blaine specific surface of approximately 3500 cm²/g, which is the value for the cements currently on the market in Reunion Island.

The reason for "co-grinding" materials for a fixed duration was to verify whether the use of SSCFA was more advantageous for this type of grinding in a cement plant. It allowed us to check whether better fineness and results in terms of workability and compressive strength could be obtained compared to pozzolana cement with an equivalent grinding duration. For this study, the main disadvantages of this grinding method were the difficulty of exploiting the results scientifically and making comparisons between the different cements, as only the final Blaine specific surface was known. Moreover, given the grindability differences among constituents (clinker, fly ash, pozzolana, slag and gypsum), the behaviour of each during the grinding was difficult or impossible to identify.

2.3.3. Equivalent global fineness grinding

The last method used consisted of two steps: first, separate grinding as for the separate grinding method, then co-grinding of the components in order to reach a targeted and constant global fineness (Blaine specific surface) for all the composite cements tested.

The cement with the highest expected final Blaine specific surface value, namely cement with 35% SSCFA, was the first prepared using this method. This Blaine specific surface was taken as the target value. This cement was chosen because it contained the largest amount of SSCFA, the particles of which had a specific Blaine specific surface about twice that of the ground clinker. Then, the other cements were obtained by co-grinding their respective components (after the separate grinding of each component) until the target Blaine specific surface value was reached. This method avoided sub-grinding constituents such as clinker, while ensuring a final fineness close to the same value for all cements (that is why it is referred to as equivalent global fineness grinding).

The interest here is to show the effect of replacing the clinker while keeping the same fineness for the different cements produced. The disadvantage of this type of grinding is that, depending on the co-grinding duration needed to reach the desired fineness, there is deviation from the initial fineness of the different materials, especially those for which the grindability is high. For example, a CEM II/A, which contains 83% clinker, 13% SSCFA and 4% gypsum, requires much longer co-grinding than a CEM II/B, which contains 70% clinker and 30% SSCFA (cf. part 3.2.3). This higher co-grinding duration will therefore have a direct impact on gypsum and SSCFA, which have high grindability in comparison with clinker or slag (see grindability of materials in Figure 1). This observation is discussed in more detail in the following part.

3. RESULTS AND DISCUSSION

3.1. Influence of grinding time on fineness of binder components

Figure 1 shows the evolution of specific surfaces according to the duration of grinding for the components tested. The mass introduced into the mill was arbitrarily fixed at 600 g in order to keep the same reference value for all the components tested and ensure good repeatability. After the grinding step, the specific surface of each component was evaluated according to EN 196-6.

In order to better understand the grinding behaviour of each material used for the manufacture of laboratory cements, their specific surfaces were assessed after various grinding times and the grindability was assessed from the slope of the curve. From the results presented in Figure 1, a much lower grindability can be observed for clinker, the main constituent of Portland cements, and for slag, which is very close. The pozzolana was brought back into the same range of fineness as the SSCFA after a few minutes of grinding. Gypsum was the material with the finest particles among the binders tested; it reached 10 000 cm²/g after 15 minutes of grinding.

Differences in grinding behaviour were observed in terms of both grindability and final fineness obtained. Actually, SSCFA reached a specific surface of around 8000 cm²/g after 5 min of grinding, as for gypsum. However, by looking at the slopes of their respective curves between 5 and 15 min, it can be noted that the SSCFA presented slower kinetics of grinding, which seemed to decrease further for times longer than 15 min. For pozzolana, a rather linear grinding curve was observed up to 20 min, then grindability decreased after 30 min to reach a specific surface around 8000 cm²/g. The slag and the clinker showed a linear behaviour through 80 min of grinding with a specific surface reaching around 4000 cm²/g and a slightly higher grindability for the slag.

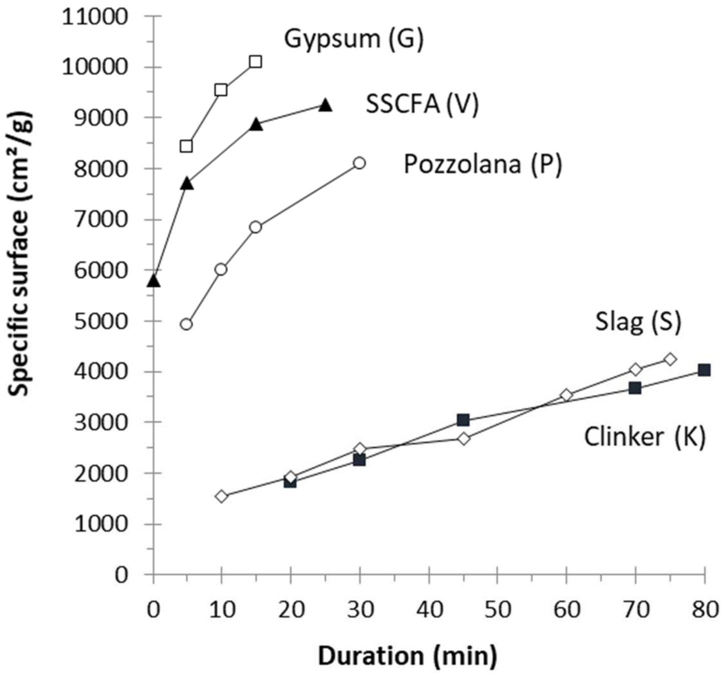

Figure 1: Specific surface versus grinding time for the materials investigated

3.2. Impact of grinding method on cement fineness through Blaine specific surface

3.2.1. Impact of separate grinding on fineness

The specific surface values of the cements manufactured by the separate grinding method are shown in Figure 2. For this method, the different materials were crushed beforehand in order to reach specific fineness objectives (cf. part 2.3.1). We recall that the pozzolana was ground to a fineness approaching that of SSCFA (5700 cm²/g). Clinker (3600 cm²/g), slag (4100 cm²/g) and gypsum (6100 cm²/g) were ground to a specific surface value considered sufficient to obtain good reactivity in the binders investigated.

Good correlation was observed between the increase of specific surface and the increase of SSCFA percentage in the different compositions. As shown in Figure 2, this was true not only for binary cements (SSCFA alone, represented by the black triangles), but also for ternary cements (SSCFA/pozzolana in red triangles) and quaternary cements (slag/pozzolana/SSCFA in purple triangles). Figure 3 also highlights this correlation by showing a linear relationship between the amount of SSCFA and the specific surface of the cement (R^2=0.99).

Moreover, it can be noted that the specific surfaces of cements with SSCFA were greater than those of cements with pozzolana (for binary cements and also for ternary cements in green triangles on Figure 2), despite the fact that the initial fineness values were equivalent for these two materials. This might be explained by the homogenization step when making the mixtures (see part 3.1), during which SSCFA, more crushable than pozzolana at this stage, would lead to a greater fineness for a given duration of grinding. The larger specific surface difference between SSCFA and pozzolana cement obtained at 30% replacement (compared to 15% replacement) seems to confirm this hypothesis.

SSCFA/pozzolana composite cements (in red triangles) tended to have higher specific surface values than SSCFA cements (in black) for different clinker replacement rates. This could be due, as for the co-ground cements, to a better granular arrangement [19], with higher specific surface here because the materials were ground beforehand.

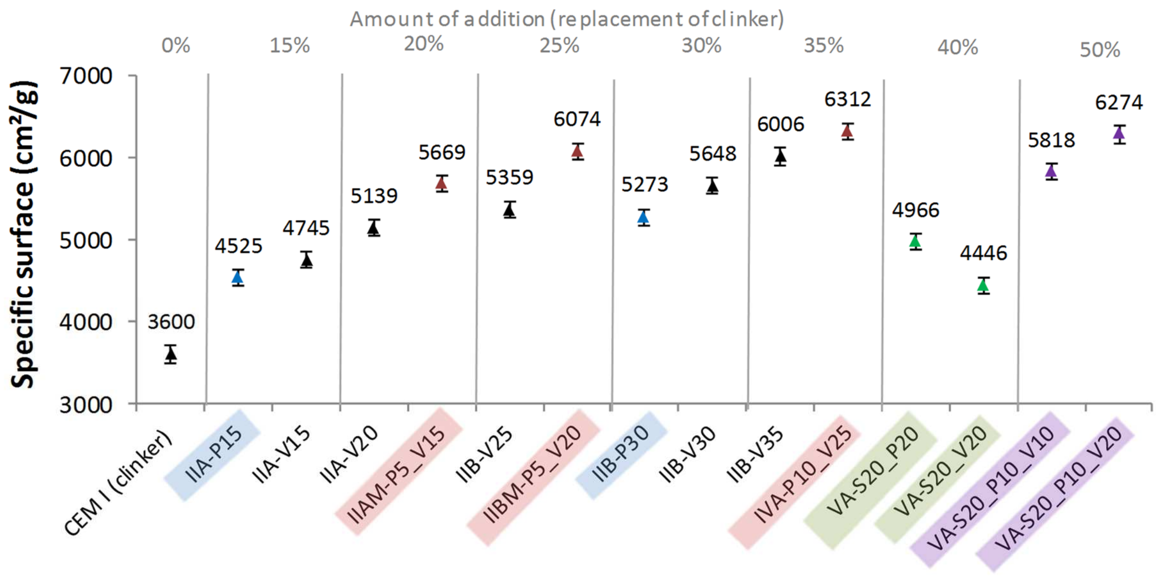

Figure 2: Blaine Specific Surface of the composite cements obtained by the separate grinding method

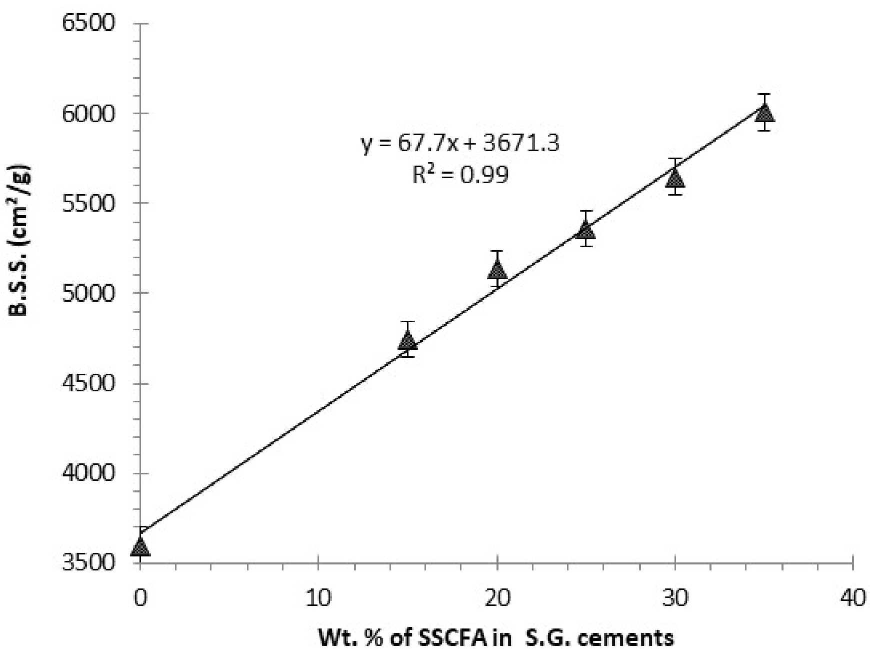

Figure 3: Correlation between the percentage of SSCFA and the Blaine specific surface of composite cements

3.2.2. Impact of co-grinding on fineness

We recall that the main objective was to achieve the same fineness as that of the CEM II/A-P15 cement commercially available on Reunion Island, which is about 3600 cm²/g. The grinding time needed to reach this value was therefore assessed. Then, the grinding duration obtained was imposed on all the other mixtures in order to evaluate the influence of the quantity and nature of additions for a fixed grinding duration.

Figure 4 presents the results of the specific surfaces obtained for 10 different cements. An increase in the specific surface was observed with the percentage of clinker replacement. This result was expected, as the clinker was less easy to grind than the other materials tested (except slag as shown in Figure 1). Therefore, its replacement during co-grinding resulted in a double effect: on the one hand, a reduction of the less grindable part of the mixture and, on the other hand, an increase of the material proportion that was easier to grind.

Higher specific surface and better grindability of cements with SSCFA (black triangles in Figure 4) than with pozzolana (blue triangles in Figure 4) were noted. The difference in specific surface was observed to be much higher at 30% replacement of clinker than at 15%. This was due not only to the fact that SSCFA are already in powder form before grinding, but probably also because their grindability is greater than that of pozzolana, as seen in Figure 1.

In addition, composite cements with both SSCFA and pozzolana (red triangles in Figure 4) tended to have a slightly higher specific surface than those with SSCFA only. However, this trend was not verified at 35% replacement of clinker. This phenomenon could be explained by a better granular arrangement of the grains, reducing the permeability of the powder bed of the mixtures during the measurement of specific surface [19, 21]. In fact, clinker is less crushable than pozzolana (cf. part 3.1), which itself is less crushable in this mixture than SSCFA (already in pulverulent form), a more compact distribution of particles could have been obtained as for a concrete granular skeleton [19].

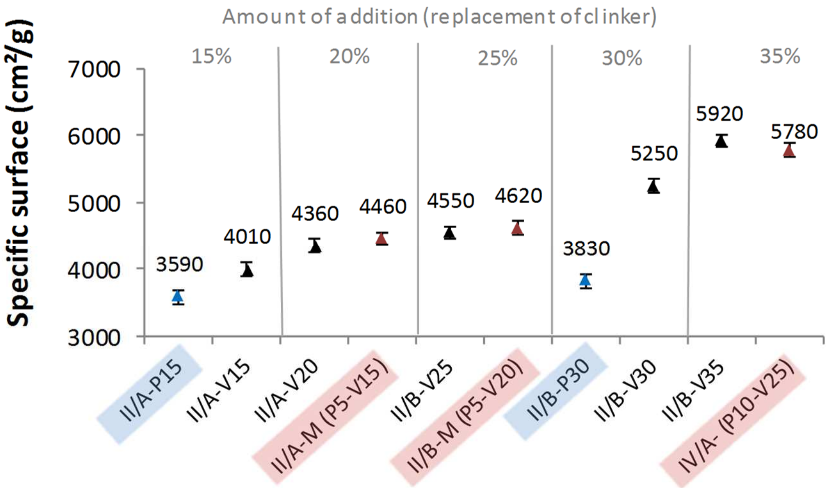

Figure 4: Blaine Specific Surface of the composite cements obtained by the co-grinding method

3.2.3. Impact of equivalent global fineness grinding

For the equivalent global fineness method, the different cements were ground to equivalent specific surfaces. The slight variation observed in fineness can be explained by the difficulty of obtaining accurate specific surface values with this method. From the results shown in Figure 5, it can be observed that co-grinding duration decreases with the clinker replacement rate and is higher for pozzolana-based cements than for those with SSCFA. It can also be noted that the amount of clinker has greater influence on co-grinding duration when cements with 15% replacement (II/A-V15 versus II/A-P15) are compared with those having 30% replacement (II/B-P30 versus II/B-V30). This result confirms the ones obtained in part 3.1 and shows the interest of using SSCFA instead of pozzolana for a substantial saving of grinding energy, as the grinding duration needs to be doubled for II/A-P15 compared to II/A-V15 cements.

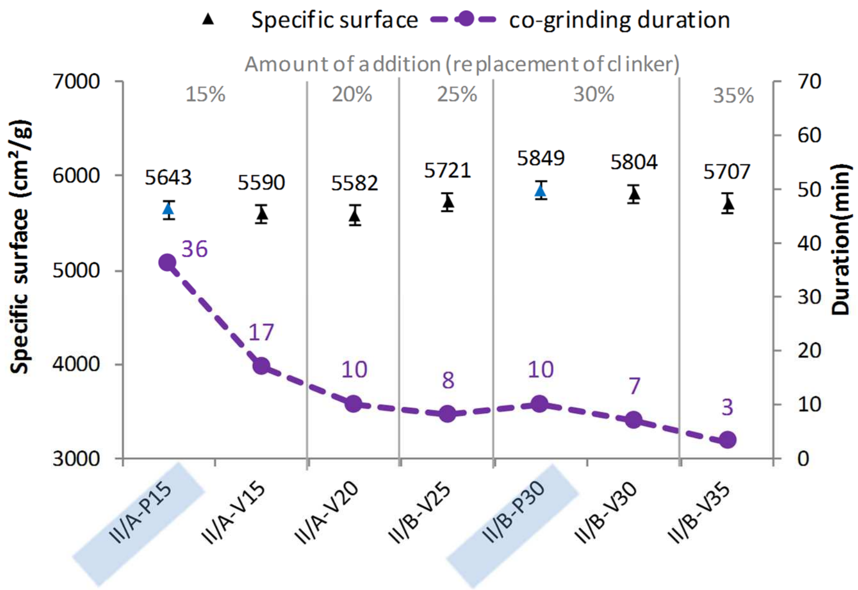

Figure 5: Blaine Specific Surface of the composite cements obtained by the equivalent global fineness grinding method

3.3. Fresh and hardening properties

3.3.1. Workability of mortars

The effect of the different components of composite cements on mortar workability was assessed by measuring the flowing time with LCL apparatus [18]. The flowing time results for mortars based on cements obtained only with the separate grinding method are shown in Figure 6. The aim here is to observe the influence of addition incorporation and nature on flowing time by increasing the percentage of clinker replacement from 0% to 50%. The results show that the replacement of clinker by addition led to an increase in the flowing time, thus reducing the workability of mortars. In fact, all the flowing times measured were longer than the one obtained for the mortar composed of CEM I (2 seconds).

An increase of 15 to 30% of clinker replacement by pozzolana (blue) did not increase the flowing time significantly. For mixtures with SSCFA (black), a large increase in the flowing time was observed for a replacement rate of 30% and 35%. In terms of workability, an upper limit of 25% for the use of SSCFA seems to be reasonable (7 seconds). At this point, using plasticizers would be almost inevitable for proper workability.

The incorporation of slag appears to be detrimental to workability, as the flowing time of ternary binders (cement/slag/pozzolana and cement/slag/SSCFA, green) were rather high (14 and 17.5 seconds respectively). For these mixtures, pozzolana was seen to have a positive effect on workability, compared to SSCFA, as it reduced the flowing time.

For the same amount of addition, the combination of pozzolana and SSCFA improved workability as it reduced the flowing time at 20%, 25%, and 35% of replacement compared to SSCFA mixtures and also at 40% compared to slag-pozzolana or slag-SSCFA mixtures.

From these observations the following main deductions can be drawn:

- Pozzolana had better workability than SSCFA even in composite cements with slag.
- Increasing the amount of SSCFA substantially increased the flowing time and thereby reduced workability. However, mixing pozzolana and SSCFA was a good compromise to maintain acceptable workability while raising the amount of replacement.
- When approaching an amount of 30% SSCFA, the use of plasticizers is necessary to maintain acceptable workability.

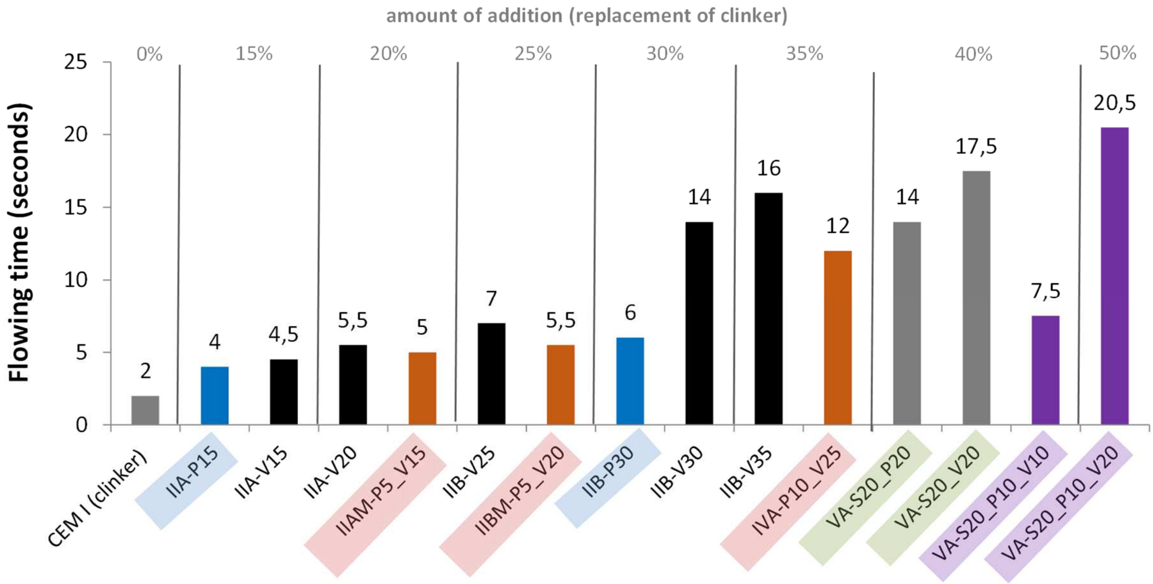

Figure 6: Flowing time of mortars made with laboratory cements

Figure 7 shows that workability (assessed through flowing time tests) is strongly correlated to the specific surface but also depends mainly on the percentage and nature of the addition (same colour code as in previous figures) used to replace clinker [20]. Actually, for the same type of addition (same colour and same shape), flowing time increases with specific surface and thus with the addition percentage, as can be seen in Figure 7. It can also be seen that green lozenges (mixes with slag) do not appear to follow the trend, with Blaine specific surface below 5000 cm²/g and flowing time above 14 seconds, showing the effect of slag combined with SSCFA or pozzolana on ternary cements. As reported in the literature [20, 22], slag behaves differently from clinker regarding the workability of cement based materials, which can explain the preceding observation.

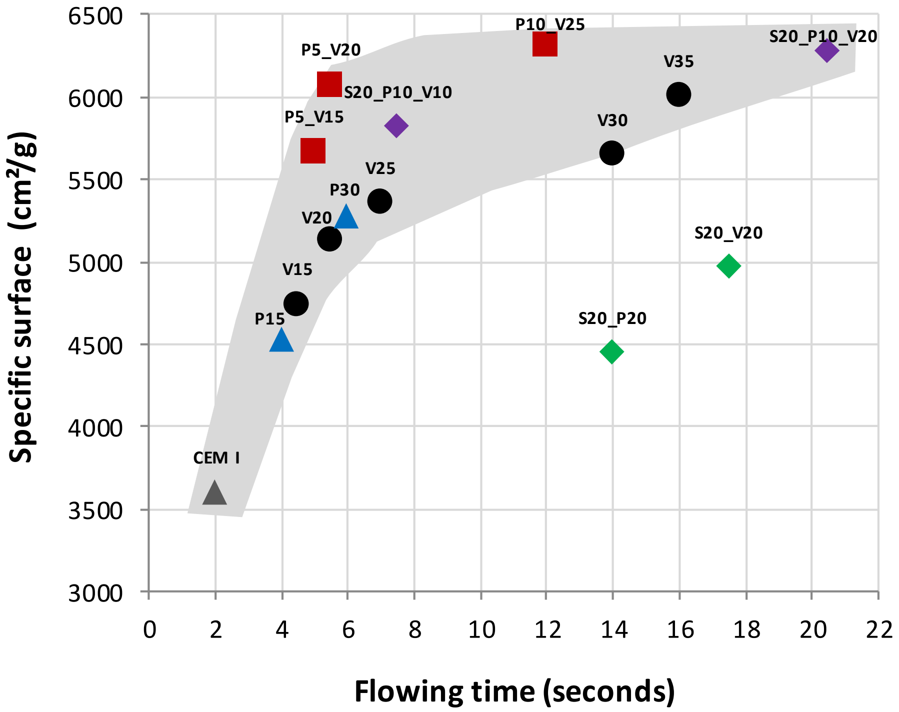

Figure 7: Blaine specific surface versus flowing time of mortars

The flowing times of different cements from different grinding methods are compared in Figure 8, where the specific surface of each cement is also plotted.

It can be noted that results with the co-grinding method are difficult to interpret due to the unknown fineness of particulate components (especially clinker and pozzolana). Despite the fact that an increase of SSCFA causes an augmentation of specific surface in cements (black filled), the flowing times are nearly the same. However, it can be seen that cements with pozzolana (blue filled), even up to 30% of clinker replacement, have less impact on workability than SSCFA does.

The equivalent grinding method shows that the type and amount of addition replacing clinker has more influence on flowing time than the specific surface of global cement. However, due to the different co-grinding durations used to obtain the final specific surface (cf. Figure 5), it can be supposed that the components' fineness (clinker, pozzolana, SSCFA and gypsum) differs from one cement to another, so interpretations cannot be linked to known components' specific surfaces. For example, II/A-V15 cement has a co-grinding duration of 17 minutes, versus 36 minutes for II/A-P15 in Figure 5; we can suppose that clinker particles will not have the same fineness in these cements.

The separate grinding method appears to be the one that can be used to identify the influence of addition ratio and addition nature on the flowing time linked to the specific surface. The principal advantage is that all parameters are controlled beforehand and known for all composite cements.

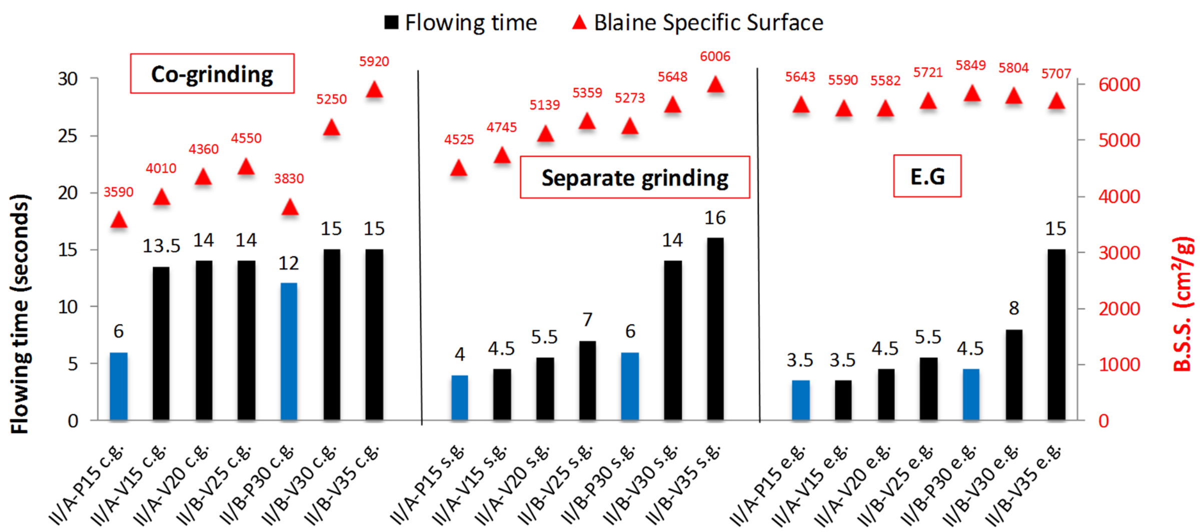

Figure 8: Comparison of flowing time for mortars based on cements obtained from different types of grinding methods (C.G= co-grinding; S.G= separate grinding; E.G= equivalent grinding) and Blaine Specific Surface (B.S.S.) values of cements

3.3.2. Setting time on cement pastes

Figure 9 presents the results of water/cement (W/C) ratio to achieve standard consistency (left y-axis) and setting time (right y-axis) in tests according to EN 196-3. When comparing pozzolana (blue triangles) with SSCFA (black dots), it is noted that, to achieve a standardized consistency, the SSCFA require more water than pozzolana, which is in accordance with previous results (cf. part 3.3). It is also in accordance with part 3.3 that slag appears to consume less water than the SSCFA, as there is a lower standardized consistency for ternary cements (in green) containing 40% replacement than for II/B-V30 (30% replacement).
An increase in setting time is observed following the decrease in clinker content, which could be explained by:

- a dilution effect on the cement since the pastes with composite cements have less cement than the reference, resulting in a decrease in the quantity of hydrates formed in the first few hours [14, 23];
- an increase of the water-cement ratio due to the higher water demand of cement with more addition, known to have an effect on the setting time [13, 14, 23];
- a harmful effect of the ashes themselves, maybe due to the presence of minor elements (e.g. P, Zn, etc.) perturbing the hydration of the cement [24].

There is a sharp increase of initial setting time at 30% replacement regardless of the substitute material. SSCFA compared to pozzolana, at this replacement rate, do not cause an increase in setting time despite the increase in W/C ratio; the cement dilution effect seems to be the overriding factor. However, this phenomenon could be also explained by the effect of small particles of SSCFA on the nucleation sites for hydrates, helping to increase the global hydration of cement particles and thus compensating for the delay in setting time despite the higher W/C [23, 25].

If we compare the V/A-S20V20 paste with II/A-V20, a strong increase in setting time is observed. The use of slag to replace 20% of clinker almost doubles the initial setting time, although there is no increase in water demand to achieve standard consistency. Slag appears to cause an additional delay in setting time in accordance with the literature [20-22]. Measuring pH values could also be a way to assess the role of the slag in these cements.

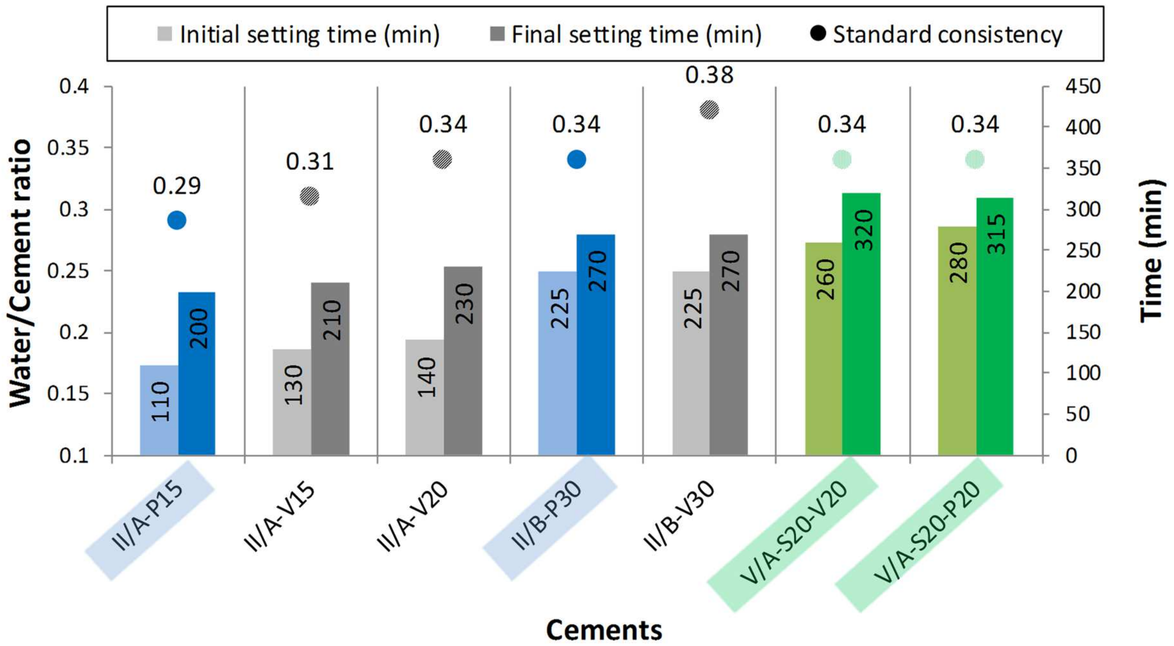

Figure 9: W/C ratio at normal consistency and setting time values obtained for cement pastes according to EN 196-3

3.4. Mortar compressive strengths

The compressive strength results of mortars made with composite cements are reported in Figure 10. We recall that, in all cements, the clinker had a Blaine specific surface around 3600 cm^2/g and the pozzolana had nearly the same Blaine specific surface as the SSCFA (around 5700 cm^2/g). From the results obtained, various observations can be made.

First, all the compressive strength values (at 7, 28 and 90 days) of SSCFA mortars (grey colour) are higher than those of pozzolana mortars (blue colour) with equivalent amounts of clinker replacement. This could be explained by the high water absorption of SSCFA particles, which reduces the W/B ratio and thus improves the mechanical performance while it deteriorates mortars in the fresh state. Replacing pozzolana by SSCFA also has a positive impact in ternary cement (green colour). However, increasing the amount of SSCFA reduces the compressive strength significantly when the replacement rate exceeds 30%.

The mix of pozzolana and SSCFA seems to improve compressive strength values, for 20%, 25% and 35% of clinker replacement, as the composite cements with pozzolana + SSCFA (red colour) always present higher compressive strengths. Observations of the strength of cements with a quantity of SSCFA set at 20% revealed that the replacement of 20% clinker by slag (II/A-S20_V20) or 5% of clinker by pozzolana (IIBM-P5_V20) kept the strength in the same order of magnitude as for II/A-V20.

Thus, the use of the slag definitely seems to be a good solution to reduce the amount of clinker while maintaining good mechanical strength. The delay observed in setting times did not seem to have a significant effect on later age strength. Compared to compressive strengths at 28 days, the trends for the other ages were almost the same.

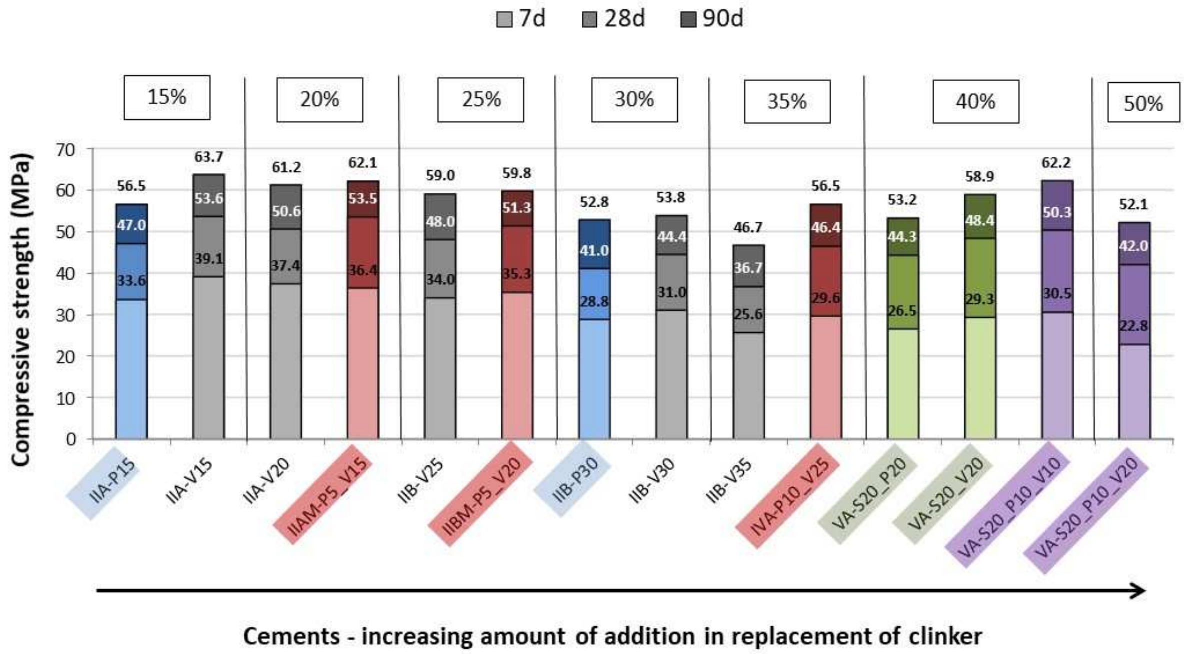

Figure 10: Compressive strength of mortars made with the manufactured cements at 7, 28 and 90 days

The 28-day compressive strength results in Figure 11 show that mortars made with cements containing up to 25% of SSCFA in replacement of clinker have better compressive strength than mortars with cement II-A/P15 (taken as the reference). These cements could be classified in the 42.5 category according to EN 197-1, as the compressive strengths are well above 42.5 MPa.

The benefits of SSCFA are also observed in cements containing 30% and more of clinker replacement. Only II/B-V35 presents a lower compressive strength than the reference, II/B-P30, but it could still be considered as a cement of class 32.5 according to EN 197-1. This reduction in strength may have been caused by settlement problems (mortar not enough fluid to be perfectly set in the mould) in the fresh state because of excessive water consumption by the increasing amount of unburned SSCFA particles present when exceeding 30%, as no plasticizer was used in this study. This settlement issue probably induced additional porosity in the mortar samples.

It is also notable that mixing SSCFA with pozzolana and/or slag enables the 42.5 MPa class of compressive strength to be achieved with up to 40% of clinker replacement.

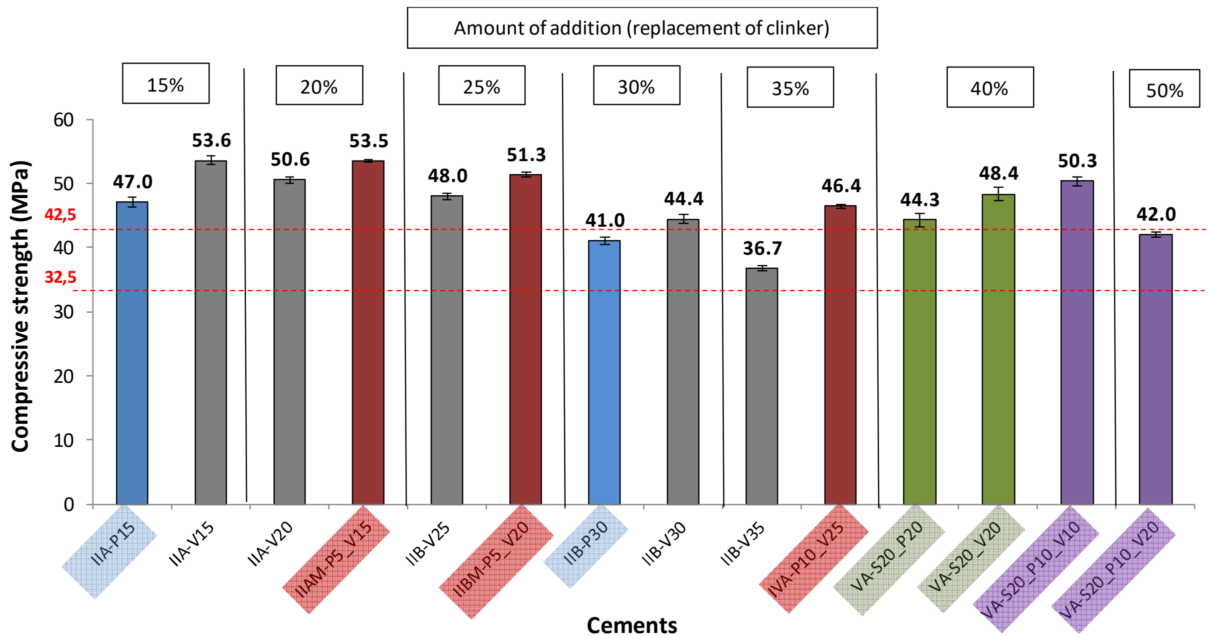

Figure 11: Compressive strength of mortars at 28 days

3.5. Predictive approach using artificial neural networks

A predictive approach to manufactured mortar compressive strength data was set up by implementing artificial neural networks. The composition and calculation principle of Artificial Neural Networks (ANN) based on the multilayer feed-forward type of neural networks (cf. Figure 12) can be found in the literature [26-28]. The objective of this approach was to be able to predict characteristics such as the 28-day compressive strength of composite cements without having to manufacture them.

The database used for this study contained 31 cements: 19 for the learning (training) database and 12 for the validation base. As shown in Figure 12, the input layer parameters were the weight ratios of clinker, gypsum, pozzolana, SSCFA and slag, and the cement specific surface. The compressive strength at 28 days was the output layer. Because of the difference of scale and units for the input and output layers, all the parameters were normalized to values between 0 and 1 by adjusting the maximum value for each parameter to 1 and the minimum value to 0, and then proceeding by simple calculation for the intermediate values.

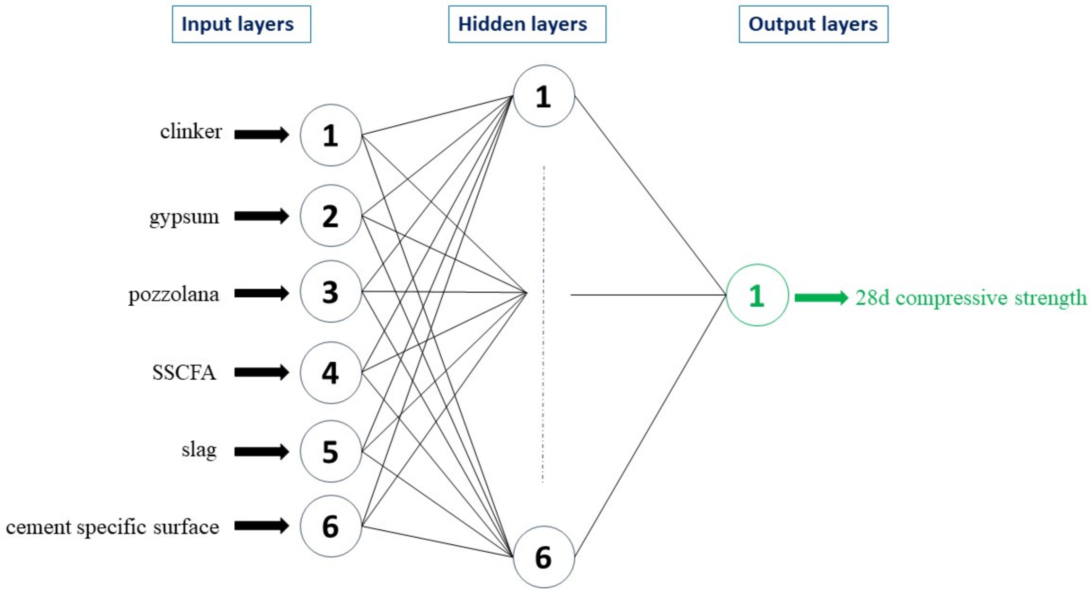

Figure 12: Structure of ANN used to predict 28-day compressive strength

Figure 13 illustrates the correlation between predicted 28-day compressive strength values and actual ones. The results show that the proposed neural network was successful in learning the relation between the different input parameters and the output parameter via compressive mortar strength.

Figure 14 shows the deviation in MPa between the predicted and measured values. A fair prediction of the 28-day compressive strength could be seen, with deviations for all the results not exceeding ±2 MPa and more than two thirds of the results presenting an error of less than 1 MPa.

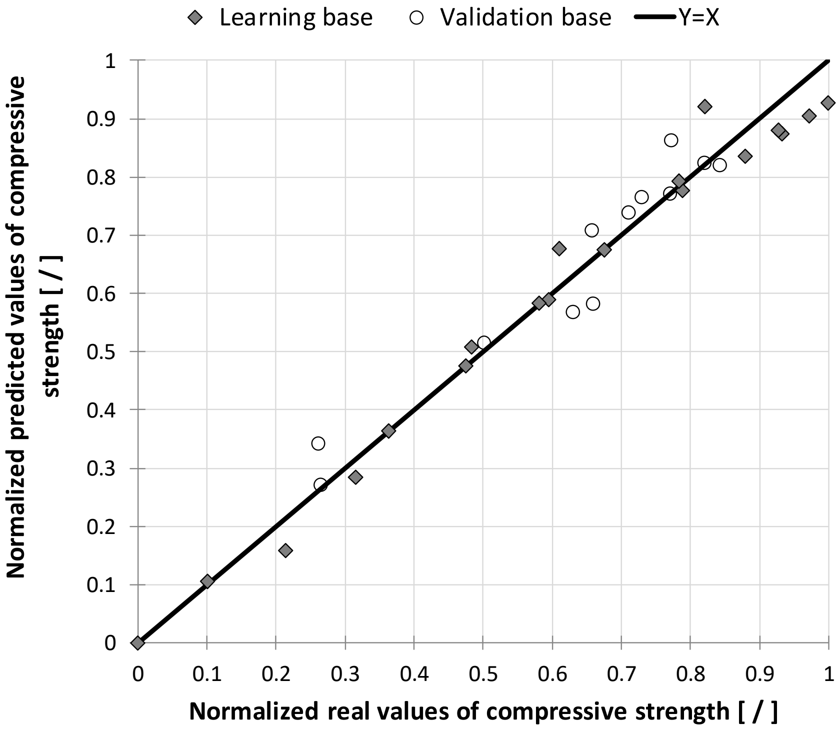

Figure 13: Correlation between predicted compressive strength and actual values

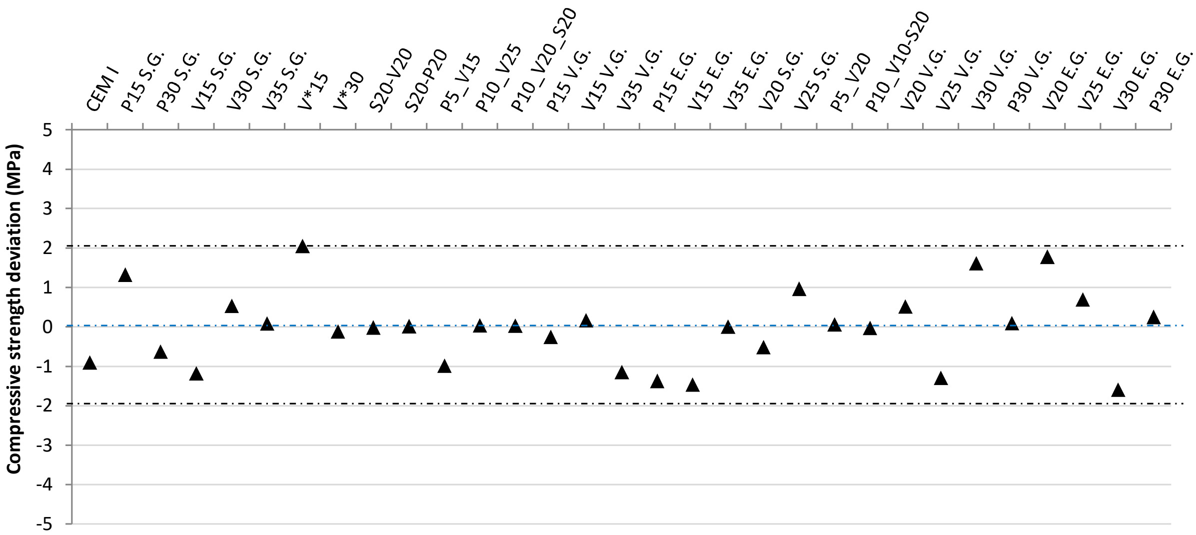

Figure 14: Deviation in MPa between predicted and actual values of 28-day compressive strength for mortars

This approach permitted the development of response curves predicting the 28-day compressive strength of mortars with three kinds of compositions according to the clinker content, as shown in Figure 15. It can be seen that:

- With fly ash alone in replacement of clinker, there is a marked fall of compressive strength following the reduction of clinker.
- The mix of fly ash with pozzolana in ternary cements limits the fall of compressive strength when the amount of clinker in the mix is reduced.
- The amount of clinker can be lowered by using slag and keeping the amount of fly ash the same, at almost 20%.

The response curves presented in Figure 15 also enable a class of cements (compressive strength) to be targeted according to the type of mix and amount of clinker replacement.

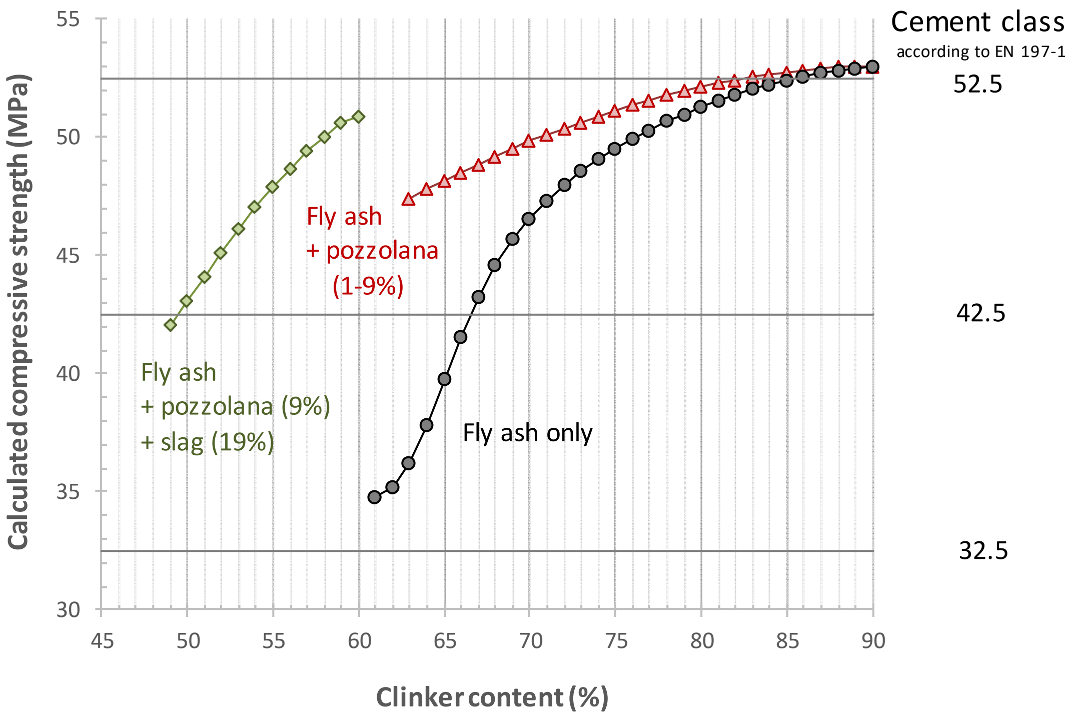

Figure 15: Response curve for 28-day compressive strength of cements with fly ash only, fly ash + pozzolana (1-9%) and fly ash + pozzolana (9%) + slag (19%) following clinker content

4. CONCLUSIONS

The main objective of this paper was to illustrate how circular economy could be applied in the development of cement-based matrices with Spreader Stoker coal fly ash. **In this context, the first step was to evaluate, from a technological point of view, the advantages or disadvantages compared to natural pozzolana, which is currently the only material used as a replacement for clinker in cement manufacturing on Reunion Island**. Ternary and quaternary cements were also made to evaluate some combinations between ashes, natural pozzolana, and blast furnace slag.

The main conclusions that can be drawn from these results are:

- **Making cement is easier with SSCFA than with pozzolana**. Since SSCFA are already in pulverulent form, they make it possible to save on grinding duration and gain in overall fineness of the cement manufactured. **They could also be used as a grinding agent in the case of co-grinding with clinker, which would represent a significant economic advantage**.

- Three types of grinding methods have been investigated: separate grinding, co-grinding and a combination of these two, in order to understand their effects in manufactured cements. Separate grinding is the method that gives the best understanding of the effects of individual components because it provides the capacity to control the initial fineness of each constituent of the cement. It was therefore the method investigated for cement paste and mortar results in order to analyse the effects of components in the laboratory-manufactured cements.

- In the fresh state, SSCFA degrade the rheological properties of cement-based matrices with respect to the properties obtained with pozzolana. This degradation is, however, less marked when the clinker replacement rates are lower than 30%.

- In the hardening state, the lengthened setting time also seems to be an effect induced by SSCFA rather than a clinker dilution effect.

- **SSCFA showed better mechanical performance than pozzolana**. The results also showed good interaction between the fly ashes and slag, making it possible to replace up to 40% of clinker while improving the mechanical strengths compared to mixtures with 30% replacement. **There was also good interaction between SSCFA and pozzolana, which could be a good compromise to limit the negative effects of SSCFA on rheology while maintaining a replacement rate of over 30%**.

- **A predictive computing approach with artificial neural networks provided good predictions of 28-day compressive strength values of laboratory-made cements** with known compositions and components finenesses and permitted response curves to be drawn for mixes according to clinker content, in order to target a class of cement as defined in EN 197-1.

Acknowledgements

The authors are grateful to CICM and Albioma for their financial support.

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