Eco-efficient concrete produced with a new amorphous hydraulic binder with C/S molar ratio of 1.1 – proof of concept in mortar mixtures

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ABSTRACT

The development of more sustainable cementitious materials is a constant challenge, driven by the environmental responsibility and need to reduce anthropogenic carbon dioxide emissions during the next decades. Recently, a new amorphous hydraulic binder was developed by the CIMPOR-Instituto Superior Técnico partnership that emerges as potential alternative for the OPC clinker. This new product has a CaO/SiO_2 (C/S) molar ratio of 1.1, having the potential of reducing CO2 emissions in about 25% in comparison with the traditional OPC. In the present thesis, mortar mixtures were produced for the first time with the new amorphous binder, and a comparative analysis was performed with mortar mixtures produced with Ordinary Portland Cement (OPC). For the present characterization the following tests were performed: fresh state characterization tests, mechanical strength tests at the ages of 3, 7, 28, 56, 91 and 120 days, shrinkage evolution tests until the age of 91 days and SEM images. It was possible to characterize the new amorphous binder in its fresh and harden state and identify the parameters that must be corrected in order to obtain a high quality construction material. The results are promising, especially when the new amorphous binder is alkali activated with a small percentage of a sodium silicate and sodium hydroxide aqueous solution, which allows it to have strength resistances of the order of magnitude of the OPC ones. These first results obtained with macro-scale mixtures, reveal that this alternative might arise in the future as a beneficial option to the OPC clinker in many specific applications.

Keywords: Amorphous hydraulic binder, clinker, alkali activation, mechanical strength, shrinkage.

1. INTRODUCTION

Concrete, mortar and pastes are worldwide used in the construction industry, being therefore Portland Cement (Ordinary Portland Cement – OPC) the most consumed product, immediately after water. In 2017, 4.100 million metric tons of cement were produced all over the world, making this industry responsible for 6-8% of the global anthropogenic CO_2 emissions [1]. It is estimated that, using the best available technology, about 800 kg of CO_2 are emitted to the atmosphere for each ton of clinker produced [1]. This gas is emitted from the calcination process of limestone, from combustion of fuels in the kiln and from power generation for purchased or self-generated electricity [2]. Carbon dioxide is a greenhouse gas present in the Earth atmosphere, but since the Industrial Revolution, anthropogenic emissions have rapidly increased leading to global warming, among other problems. A new study of Moody's Investors Service indicated that the search for this material can increase between 12 and 23% until 2050 [3]. The challenge is to reduce CO2 emissions and simultaneously increase production, pushing the industry to reduce CO2 emissions in the production process. After the Paris Agreement in 2015[4] future taxing of CO_2 emissions is a reality and the industries need to adapt. The most direct way to reduce CO_2 emitted by the cement industry is to develop new clinkers with a smaller amount of carbonated raw materials needed. However, Portland cement clinker is highly dependent on the chemistry of calcium, with its main constituents containing large amounts of this element; they are the Alite (C_3S), the Belite (C_2S), the tricalcium aluminate (C_3A) and the tetracalcium aluminoferrite (C_4AF). Unfortunately, calcium is usually found in nature in its carbonated form of limestone (CaCO3), being its calcination process responsible for about 60% of the total CO_2 emissions of the entire cement production process.

The CIMPOR-IST project is active since 2012 trying to be a leading investigation and role model in developing more sustainable cements to introduce in the industry. The initial objective was to investigate the hydraulic properties of amorphous clinkers with C/S<2 in order to find a new family of alternative environment-friendly clinkers. As a result, two patents have been developed for dendritic belite based hydraulic binders [5] and for low calcium content amorphous hydraulic binders [6]. In the follow up of this project several works have already been develop and published: three master thesis [7–9], a PhD thesis [10] and several scientific papers [11–15]. The new amorphous binder C/S 1.1 studied in this work, reduces in about 33% the amount of CO2 originated from the raw mix in the production process.

Previous studies demonstrated an elevated increase of strength in pastes produced with alkali activation. The one that presented the best results to date was an aqueous solution containing Na_2SiO_3 (sodium metasilicate commonly known as water-glass) corrected with an addition of NaOH to obtain Si/Na molar ratio of 1.2 [12]. In the investigation developed, a notorious difference of water/cement ratio, *w/c*, was noticed in order to obtain a fluid-plastic workability in both cement pastes (about 0.325 for the amorphous binder and 0.40 to 0.45 for OPC). It's well-known the influence of the *w/c* ratio variation in the mechanical strength of the OPC mixtures but, in the amorphous binder mixtures, the amorphous efficiency is much higher for lower *w/c* ratios and has the tendency to drastically lose its mechanical performance with its raise. This factor anticipates strong difficulties in finding a good compromise between mechanical performance and good workability in mortar and concrete mixtures of the amorphous binder, because the high volume of aggregates require an increase of *w/c* ratio In OPC mixtures, this compromise of good workability and low *w/c* ratios are compensated with the use of water reducing admixtures. With that said, it was important in this work to introduce the use of this admixtures in the mixtures produced with the new amorphous binder.

In the present study the goal of formulating current concrete mixtures, with three types of OPC cements from CIMPOR and with the new amorphous binder, was established, having this formulations been converted to the respective mortar mixtures, taking out the respective proportion of larger aggregates and normalizing the proportions of the other constituents to the unitary production volume. With the OPC cements, the concrete mixtures were also produced in order to correlate both mixtures and withdraw conclusions and future developments.

2. MATERIALS, FORMULATIONS AND PRODUCTION CONDITIONS

2.1. Amorphous hydraulic binder

The raw materials used in the production of the low calcium content amorphous C/S 1.1 are the ones typically used in the production of Portland cement clinker. Limestone is the main source of CaO, sand is the main source of SiO_2 and Fuel Catalytic Cracking (FCC) is the source of SiO_2 and other minor constituents such as Al_2O_3 or Fe_2O_3. The clinker production is limited to the laboratory scale at this moment. Table II.2 I presents the raw materials compositions determined by X-ray fluorescence (FRX) of the material samples used in this study to produce the amorphous binder clinker. The raw materials are milled and mixed to produce the raw-meal that is then placed in a platinum crucible and melted at a temperature of 1550 °C to ensure homogenization of the material composition. The melt is then cooled rapidly in water to obtain a hydraulically active material. Finally, the material that came out of the furnace was ground in a ring mill for 180 s with propanol, followed by a drying step at 50 ºC in an oven for about one hour

Table 2.1-I-Final amorphous binder composition.

	SiO_2	Al_2O_3	Fe_3O_3	CaO	MgO	SO_3	K_O	Na_2O
%	47.49	1.98	0.14	49.67	0.15	0.00	0.66	0.08

After leaving the furnace, the clinker is almost 100% amorphous, containing only two crystalline phases, called Wollastonite (β-CS) and Pseudowollastonite (α-CS). The amorphous binder has no additions, so it is 100% clinker, and has a Blaine surface of 5130 cm^2/g. For a better understanding of the difference to the traditional Portland cement, its typical composition contains 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% of other minor compounds [16]. From this composition the four main crystalline phases of the clinker previously mentioned are formed, the Alite, the Belite, the tricalcium aluminate and the tetracalcicium alumino-ferrite. Portland cement clinker is manufactured in a rotary kiln that reaches temperatures in the order of the 1500 °C, where a partial melting of the material occurs and where clinker stones are formed. Then they are milled and mixed with additions to form the various types of traditional cements that currently exist [17]. Besides the significant differences in the composition between the amorphous binder and the OPC, there is still a notable difference in the *w/c* ratio required to obtain good workability in the mixtures performed with both materials.

2.2. OPCs used in this work

Three types of OPC produced by CIMPOR were selected for the present study and analyzed according to the CIMPOR-Alhandra cement plant production quality tests. X-Ray Diffraction with Rietveld analysis was also performed in order to identify all the cement constituents, being all in agreement with the EN 197-1:2001 [19] standard. The OPC used and the respective constituents were: (i) CEM I 52.5R, with a density of 3.11 kg/dm^3, with 95% clinker and 5% gypsum, and with a Blaine fineness of 4390 cm^2/g, ensuring a high strength cement characteristics; (ii) CEM II A/L 42.5R, with a density of 3.09 kg/dm^3, with 83% clinker, 13% limestone filler and 4% gypsum, and with a Blaine fineness of 4490 cm^2/g; (iii) CEM II B/L 32.5N, with a volumetric density mass of 2.98 kg/dm^3, with circa 67% clinker, 29% limestone filler and 4% gypsum, and with a Blaine fineness of 4580 cm^2/g.

2.3. Aggregates, water and admixture

The aggregates selection for the design of the concrete mixtures and corresponding mortar mixtures was made in order to accomplish stable and homogeneous mixtures, with an adequate compactness and workability. The following aggregates were adopted: fine silica sand 0/1 mm, medium silica sand 0/4 mm and silica gravel 4/8 mm, all with a density of 2.63 kg/dm3 and a medium limestone gravel 6/14 mm, with a density of 2.66 kg/dm3. In the production of mortars, only silica sand and gravel were used. Water used from the public water supply network of Coimbra was used in the mixtures production and the selected admixture was a superplasticizer by BASF, named MasterGlenium Sky526 (MGS 526).from BASF.

2.4. Mixture formulation

The method used in the present work was the methodology proposed by Lourenço et al [18] both for normal and lightweight aggregates concrete. The paste components were initially adjusted (compactness, air content and cement dosage), being the complementary volume the aggregates volume distributed by the proportions obtained from the adjustment of the aggregates granulometric curves, *Figure 2.4-I,* to Faury's granulometric reference curve [18], *Figure 2.4-II*. Small adjustments were made to the reference curve's parameters so that the volume of coarse aggregates was equal to 35% for all the different formulated concretes. Therefore, the formulation of the respective mortar mixtures results from the division of the dosages of the constituents (except the coarse aggregates) of the concretes by the complementary proportion of 65%.

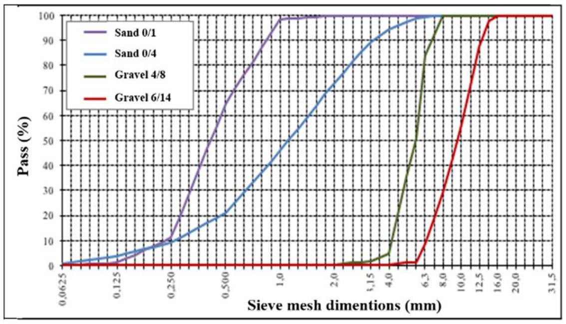

Figure 2.4-I – Granulometric curve of the aggregates.

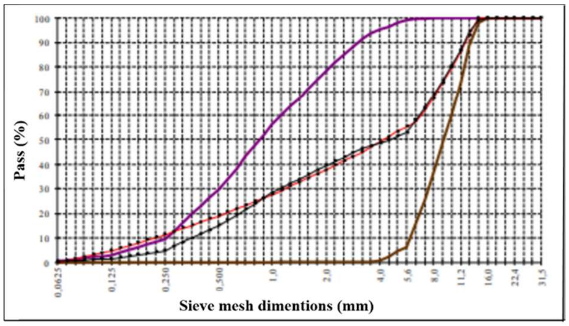

Figure 2.4-II- Ajustment to the Faury's reference curve.

The production of the amorphous binder clinker is still limited to laboratory scale and thus only very small batches can be produced. For this reason, it was decided to settle the clinker content to 300 kg/m³or lower, for all mixtures prepared. Although increasing the cement content would allow better workability of the mixtures with reduction of the water/clinker ratio (*w/clk*), enhancing the efficiency of the amorphous performance. It should be noted that with the incorporation of the aggregates, the *w/c* ratio must be adjusted to values higher than the pastes, due to the water absorption by these components. This happens in mixtures of OPC and of amorphous binder, although with greater difficulty in the second case, because of the low optimum *w/c* ratio value and to the greater loss of strength performance with the increase in this ratio. It is important to emphasize the idea that with a higher clinker content, this difficulty would be attenuated because it would be possible to maintain the w/c ratio, empowering the improvement of efficiency of mechanical strength.

2.4.1. OPC mixtures

Regarding OPC mixtures *Table 2.4-I*, two different series have been considered. In the first series the type of OPC used varied, being the mixtures called C5, C4 and C3 (with CEM I 52.5R, CEM II A/L 42.5R and CEM II B/L 32.5N, respectively), keeping constant the clinker content, equal to 300 kg/m³, and the *w/clk* ratio, equal to 0.565. The compactness was settled as 0.81 and the air content as 2%, being the superplasticizer content used very low (0.2% of the cement mass). The second series was mix designed with the variation of two cement types, being the mixtures called C5 and C3A (with cements CEM I 52.5R and CEM II B/L 32.5N, respectively), maintaining the cement content equal to 316 kg/m³ and the w/c ratio equal to 0.536. The compactness and air content defined and the amount of superplasticizer used were the same as in the previous series.

In the mix design of the first series, in which a constant clinker content of 300 kg/m³ was used, the content of cement increases from C5 to C4 and to C3 (and the *w/c* ratio decreases), because with the reduction of the cement strength class the percentage of clinker in the composition of the cements decreases as well, as explained in *section 2.2*. The decision of using a constant clinker content in this series is based on the fact that the amorphous binder is 100% clinker. This decision is expected to influence the strength evolution of this series since, on one hand, C5 (CEM I 52.5R) is the finest cement and thus with the highest strength and, on the other hand, the increase of cement content (with constant clinker) provides an increase in workability and compactness with a consequent improvement of mechanical performance. The decision was made with the objective of comparing the amorphous binder with the Portland cements, maintaining constant the parameter that influences most the mechanical strengths, i.e., the clinker content. The content of the superplasticizer, being dependent of the cement content, allowed mixtures to have the same *w/clk* ratio and to reach the adopted consistency class: plastic consistency (S4).

The mix design of the second series had the main goal of providing an objective comparison with the amorphous binder, using a constant cement content. In this case, there was an advantage from the already produced C5 mixture, which has a clinker content of 300 kg/m³ and a consequent cement content of 316 kg/m³, being complemented with the new C3A mixture with the same cement content of 316 kg/m³ and a consequent clinker content of 212 kg/m³. This comparison was made using the most different cements in a strength and composition characteristics point of view. The w/c ratio of 0.536 was also maintained constant in both mixtures. In the design of all mixtures there was a search for reaching the same consistency in all mixtures, so the superplasticizer content was decreased to 0.15% in the C3A mixture because its higher fineness provides a more plastic consistency.

Tests conducted in fresh state validated the mix design parameters and allowed to move on to the following experimental characterization of the mortar mixtures. The results of these tests are showed in *Table 4.1-I.*

2.4.2. Amorphous hydraulic binder mixtures

In the amorphous binder mix designs, *Table 2.4-I*, a major difficulty to reach the right consistency with these mixtures was anticipated, regardless the fact that the amorphous binder is a finer cement than the OPC, it is more efficient with lower *w/c* ratios and the aggregates represent a major volume of the mixture which difficult workability. In addition, some of the most important parameters for the amorphous mixtures formulation were unknown, taking into account that this work is pioneer in these mixtures characterization, in particular the ideal *w/c* ratio to reach a good workability and controlling the resultant air content in the mixtures. In the first amorphous binder mixture, the cement content (which in this case is the same as the clinker content) of 300 kg/m³ was maintained and the following parameters were adjusted experimentally, observing the rheology of the mortar mixture. Once the workability was confirmed, a subdivision in two mixtures was made with the objective of being able to reduce the *w/c* ratio and maintaining the same consistency of the mixtures without compromising the amorphous binder properties (it should be noticed that these admixtures had never been used with this cement before): (i) CA_0,45 mixture of amorphous binder with a *w/c* ratio of 0.45; (ii) CA_0.40 mixture of amorphous binder with 0.2% of superplasticizer (percentage of the cement mass) that allowed the decrease of *w/c* ratio to 0.4.. Besides this effort to improve the mixtures consistency, it was verified that both mixtures still had worse slump flow in comparison with the OPC ones and the air content was much higher, which lead to a reduction of the compactness in the formulation parameters resulting experimentally in a loss of mechanical performance. The third mixture was of alkali activated amorphous binder, using a $NaOH/Na_2SiO_3$ aqueous solution defined to have a Si/Na molar ratio of 1.2 and the amount of activator added was 3% in weight of Na*2*O content, with the same cement content of 300 kg/m³ and a *AA/c* ratio of 0.4 as explained before.

Table 2.4-I- Final constituent content of mortar mixtures formulated.

Constituents. [kg/m³] and parameters.	***C5***	***C4***	***C3***	***C3A***	***CA_0.40***	***CA_0.45***	***CAA***
CEM I 52.5R	316	----	----	----	----	----	----
CEM II A/L 42.5R	----	361	----	----	----	----	----
CEM II B/L 32.5N	----	----	448	316	----	----	----
Amorphous binder	----	----	----	----	300	300	300
Water	169	169	169	169	119	135	110
Admixture (MGS 526)	0.63	0.72	0.90	0.47	0.60	----	----
NaOH	----	----	----	----	----	----	8
Na_2SiO_3	----	----	----	----	----	----	34
Fine sand 0/1	189	181	163	186	205	202	198
Medium sand 0/4	754	723	652	745	820	810	792
Coarse sand 4/8+ Medium Gravel 6/14	930	930	930	930	930	930	930
Compactness	0.810	0.810	0.810	0.810	0.845	0.840	0.860
W/C	0.536	0.468	0.378	0.536	0.400	0.450	0.380
W/Clk	0.565	0.565	0.565	0.801	0.400	0.450	0.380
AA/C	----	----	----	----	----	----	0,400
Clinker [kg/m³]	300	300	300	212	300	300	300
Air content [%]	2.0	2.0	2.0	2.0	3.5	2.5	3.0

3. PRODUCTION AND CHARACTERIZATION

Mortar mixtures were produced and characterized according to the standards NP EN 196 [19] and NP EN 1015 [20], respecting the formulation of the corresponding concrete; to produce the respective mortar mixture, removing the fraction of the coarse aggregates (35% vol.) by dividing the dosages of the constituents by 0.65. Triple molds of 40×40×160 mm³ were used for the specimens' production and harden state characterization, *Figure 2.4-I*, both mechanical strength and shrinkage. The OPC specimens were demolded 24 hours after production and placed immediately immersed in water at 20°C.The amorphous specimens were only demolded after 3 days to perform the first tests, and were only placed in water after 7 days, not running the risk of being damaged because they have not yet acquired sufficient strength and rigidity. The shrinkage specimens were placed in a thermo-hygrometric chamber at 20°C and 50% RH. In the fresh state, a slump test was performed for consistency and density and air content were characterized using the 1.0 dm3 air-meter according to NP EN 1015 [20], allowing to validate or adjust the formulation parameters. Flexural and compressive strength were characterized at the ages of 3, 7, 28, 56, 91 and 120 days using 2 prismatic specimens at each age. The specimens at 91 and 120 days had different curing conditions (they were in a thermo-hygrometric chamber with a RH of 50%) and therefore the results cannot be directly compared with the ones from the other ages. The evolution of shrinkage with age was measured using 3 specimens per mixture, using the measuring device equipped with compatible comparator watch. Finally, SEM images (scanning electron microscopy) of the fracture zones of the specimens were performed to evaluate the cement-aggregate bonds. These images were performed with 28 days specimens, of all the amorphous binder mixtures and the C3A mixture for comparison.

Figure 2.4-I- Prismatic specimens of a) OPC and b) amorphous binder mortar mixtures

Figure 2.4-II- Failure zone of the amorphous binder specimen.

4. RESULTS AND ANALYSIS

4.1. Fresh state characterization

Mortar mixtures were also characterize in fresh state, allowing the validation of each of the mortar mix designs previously done, being the next steps samples production and hardened states characterizations tests. Consistency results, air content (pred. – predicted and car. – characterized) and volumetric density mass (pred. – predicted and car. – characterized) are presented in *Table 4.1-I.* Amorphous binder mortars have shown to have a higher air content value than the OPC mixtures, resulting in the appearance of excessive porosity in the test specimens that influenced negatively the mechanical strength. This parameter tends to increase significantly with the addition of the admixture used, also a slight tendency of exudation was also observed. The consistency of the mortars with the amorphous binder has a higher viscosity, which has been observed in previous studies, but still presenting homogeneous, stable and workable mixtures, but with inferior slump flow than the OPC mixtures.

Table 4.1-I- Parameters of the fresh state characterization of the mortar mixtures.

Parameters	*C5*	*C4*	*C3*	*C3A*	*CA_0,40*	*CA_0,45*	*CAA*
Slump flow [cm]	18,5	18,5	18,5	19,0	13,0	12,5	13,0
Air content – pred. [%]	3,1	3,1	3,1	3,1	5,4	3,9	4,6
Air content – car. [%]	3,3	3,1	3,1	3,2	5,7	4,0	4,7
Density – pred. [kg/dm^3]	2,20	2,21	2,20	2,18	2,22	2,23	2,22
Density – car. [kg/dm^3]	2,21	2,23	2,23	2,20	2,18	2,25	2,22

4.2. Flexural and compressive strength

Figure 4.2-I (a) shows the evolution of the compressive strength results of the mortar mixtures at the age of 3, 7, 28 and 56 days. The three mixtures with the same clinker content and water-clinker ratio present very similar compressive strength results at all ages. The C5 mixture shows a much higher strength evolution between 7 and 28 days of age although the 56th day result comes closer to the other two comparative mixtures strength values. The C3A mixture, besides the fact that it has the same cement content and same *w/c* ratio of the C5 mixture, presents a 1.8 times lower compressive strength at the age of 28 days, but since the C3A mixture cement has a slower hardening evolution, this difference tends to decrease at later ages. Between the amorphous binder mortar mixtures, the CAA (alkali activated mixture) shows much higher compressive strength amplitude of values in comparison with the CA_0.40 and the CA_0.45 ones. The CAA mixture present values 3.0 times higher than the CA_0.40 mixture ate the age of 28 days. The comparison between non-activated amorphous mixtures, confirms the high influence of the water cement ratio in mechanical strengths. Just by reducing the *w/c* ratio from 0.45 to 0.40 with the help of a water reducer admixture, the compressive strength at the age of 28 days increased in 65%.

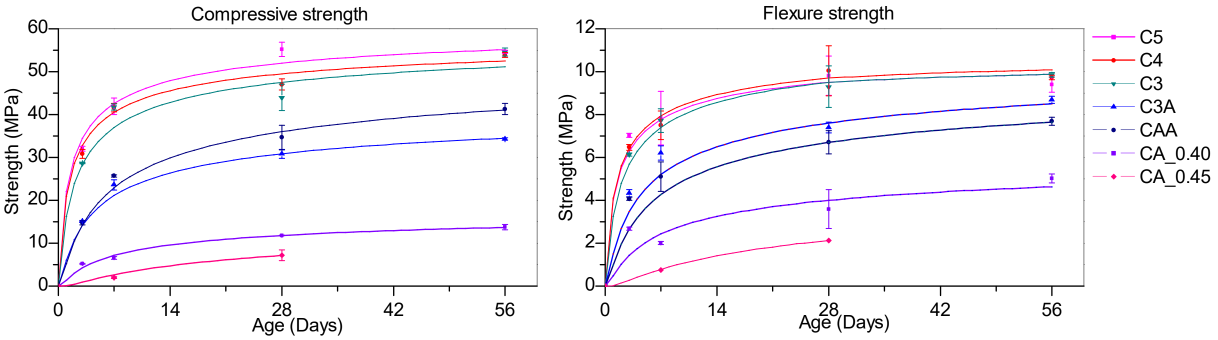

Figure 4.2-I- Compressive (a) and flexural (b) strength evolution of the mortar mixtures cured under 20ºC water.

Figure 4.2 I (b) shows the evolution of the flexural strength results of the mortar mixtures at the age of 3, 7, 28 and 56 days. Between C5, C4 and C3 mixtures, a similar behavior in the flexural strength results is verified because the clinker content and *w/clk* ratio is the same, and regardless the fact that the C5 cement has a much higher fineness, the gradual increase of cement volume in the C4 and C3 mixtures compensates that positive aspect.. As expected, these mixtures do not present any flexural strength improvement at later ages. The C3A mixture presents only a 1.3 times lower flexural strength than the C5 mixture at the age of 28 days, but also in this case this difference gets lower at older ages because of the slow hardening curve of the C3A mixture. The CAA mixture present values 1.87 times higher than the CA_0.40 mixture at the age of 28 days. The non-activated amorphous binder presents a slow hardening curve, meaning improvement of the strength values at later ages.

As explained before, flexural and compressive strength tests have been performed using specimens with different curing conditions. In fact, instead of being stores at 20 ºC in water, they were inside a thermo-hygrometric chamber with the same temperature and a relative humidity of 50%, at the ages of 91 and 120 days and, even though this results cannot be directly compared to the other ages, they provide quite relevant information. The results are presented in *Figure 4.2-II*. Both amorphous binder mixtures present lower values in flexural strength results. The higher air content of the mixtures leads to an increase of the compactness coefficient and excessive porosity, having a more negative influence on the flexural strength results than in the compressive strength ones. Also, the amorphous binder mixtures have less powder content than all the other mixtures leading to less compact and rigid mixtures. C5, C4 and C3 mortar mixtures present stabilized values after the 28 days, characteristic of rapid hardening cements. At later ages, the CAA mixture presented the best compressive strength results, because of its slow hardening curve that can be linked to its excessive shrinkage behavior, making the specimen more and more compact with time. The final result of the CA_0.40 mixture is also very good, since the strength difference for the C3A mixture was only 1.41 times lower.

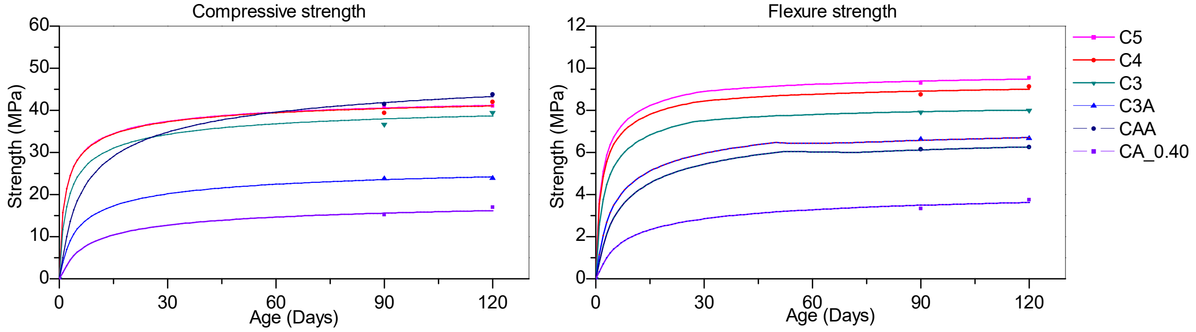

Figure 4.2-II- Compressive (a) and flexural (b) strength evolution of the mortar mixtures cured in a cabinet with 20ºC and a RH of 50%.

The higher viscosity of the amorphous binder increases the air content in the mixtures, making the air removal task much harder and energy consuming, having a negative impact in the mechanical behavior of these mortar mixtures. The mechanical strengths of the CA_0.40 amorphous binder mixture are relatively low but it is necessary to take into account the low amorphous binder content used, originating w/c ratios far away from the optimum values used in this cement pastes and also the lower amount of cement used in the mixtures. By increasing the amount of cement material, which is the most important constituent regarding mechanical properties, and maintaining the aggregates volume and its respective water consumption, mechanical strength would be higher. The analysis of these results is very promising, predicting an efficiency increase in the mechanical strength values with the reduction of the *w/c* ratio.

4.3. Shrinkage

Shrinkage results are presented in *Figure 4.3-I*, presenting the shrinkage evolution of the different mortar mixtures specimens along 91 days. The four OPC mixtures present very similar shrinkage curves, both in evolution and in range of values, which demonstrate that the shrinkage evolution in these mixtures very quickly up to 7 days, due essentially to the drying shrinkage component, attenuating its evolution after this age and tend to stabilize shortly after 28 days. C3A mixtures present values 1.15 times lower than the C5 one with the same cement content and water cement ratio, because this mixture produces less cement hydration products having 30% less clinker content. Clearly the activated amorphous binder mixture presents excessive shrinkage behavior, with values 3 times higher than the other mixtures, being this value in concordance with literature [21]. This problem and possible solution for it are well documented in experiments with AAC (Alkali-Activated Concrete) AAF (Alkali-Activated Fly ash) and AASC (Alkali-Activated Slag Cement [21,22]. The main causes of this phenomenon pointed by other authors are the activator type and content (SiO2/Na2O), the physicochemical properties of the raw materials and curing conditions [22]. Because this amorphous material is new, experiments and studies on this matter must be performed in order to find a proper solution for this problem in this specific material. On the other hand, the CA_0.40 amorphous binder mortar mixture presents a 1.5 lower range of values than OPC mixtures with the same clinker content. This may be related with the inferior amount of hydration products formed in this material, fact related with the different hydration kinetic and lower exothermic peak than the OPC mixtures.

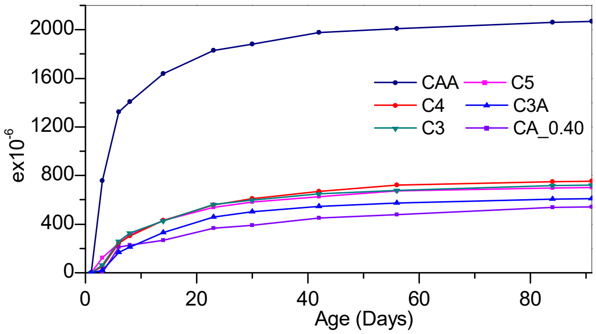

Figure 4.3-I- Shrinkage evolution of the mortar mixtures.

4.4. MEV images

Through the scanning electron microscope (SEM), high resolution images of the specimens surface of the mixtures C3A, CA_0.45 and CAA were produced *Figure 4.4-I*. In the C3A mixture, it was possible to identify the aggregates, to amplify the interface zone of the aggregates with the hydrated cement binder matrix and to observe the structure of the cement hydration products, *Figure 4.4-I a),* the images show good matrix-aggregate adhesion and reveal a low porous specimen. SEM images of the amorphous binder present higher porosity than Ordinary Portland cement mixtures with pores dimensions varying from 0.1 to 1.0 mm. Relatively high porosities of alkali activated materials are also reported in other previous studies [21]. Apart of some fractures in the matrix-aggregate bonding zones, the adherence between them seems very good. Finally, the C-S-H gel visible in the mixtures is very similar to the OPC one with a “honeycomb” structure formed by a layered mesh.

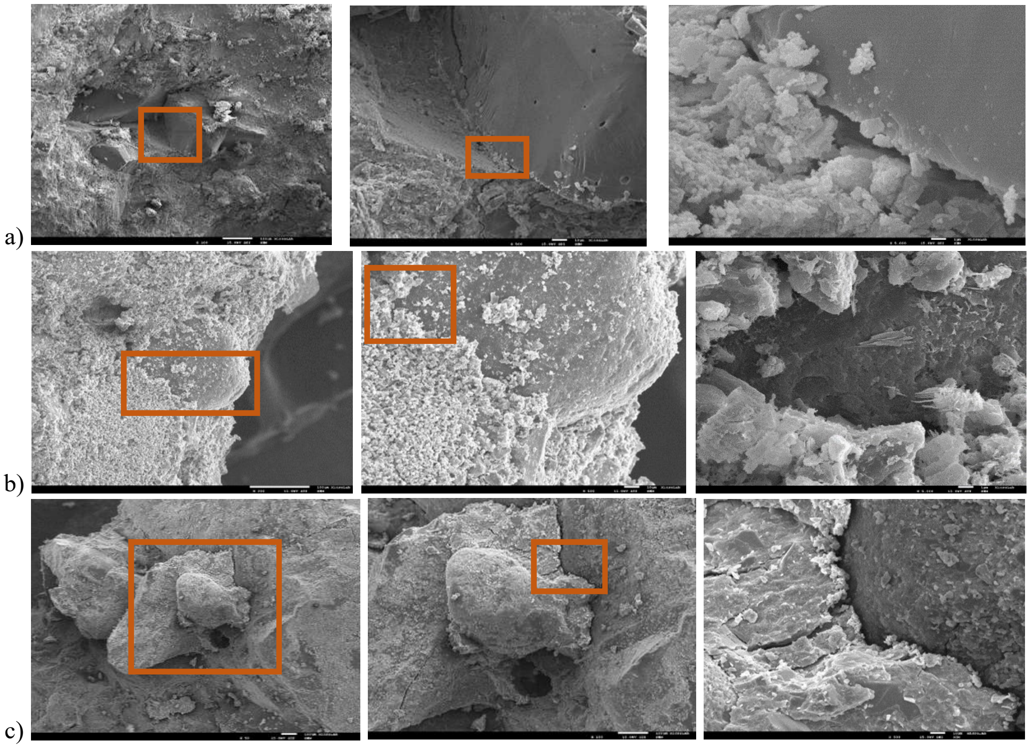

Figure 4.4-I- SEM images of the a) C3A, b) CA_0.45 and c) CAA mortar mixtures.

5. CONCLUSIONS

The present MSc dissertation aims at providing a proof of concept for an eco-efficient concrete produced with a new amorphous hydraulic binder with C/S ratio of 1.1. Since currently this new amorphous binder can only be produced in laboratory, the amount of product obtained in each batch is very small. Therefore, for the proof of concept only mortar mixtures could be produced. Then these were characterized and compared with similar mortar mixtures produced with Portland cement. Nevertheless, the following conclusions could be drawn:

- The addition of a superplasticizer in the amorphous binder mortar mixtures has revealed to be very positive. Reducing the w/c ratio and increasing workability is the key to achieve better mechanical strength values. The non-activated amorphous binder mixtures were sensitive to this crucial parameter, increasing in 65% the compressive strength value at the age of 28 days with the reduction of 12.5% of the w/c ratio. However, this addition also revealed an increase of 42.5% in the mixture air content that must be corrected in order to achieve better results.
- The amorphous binder activation with Na_2SiO_3, in a 3%wt of equivalent Na_2O content, has revealed to be as effective in increasing the amorphous binder mechanical resistances in mortar mixtures as in pastes but with a very different behavior. The hardening curve of the CAA mixture revealed to have a slow evolution, very similar to the C3A mixture one, while in pastes the activator effect in the strength improvement was immediate. It achieved values 52.8% inferior in flexural strength and 6.7% higher in compressive strength at the age of 120 days comparing to the high-resistance cement mixture C5. As negative points, this mixture presented very high air content values, 49% higher than the ones presented from OPC mixtures and shrinkage values 300% higher at the age of 28 days. It has been reported that both the incorporation of fly ashes and lowering the silicate content from activator are efficient methods to reduce the shrinkage in slag mixtures, further research must be done in this matter in order to reduce shrinkage [40].
- The SEM images of the amorphous binder mortar mixtures have revealed good aggregates-cement matrix adhesion and excessive porosity with the pours diameter dimension varying from 0.1 to 1.0 mm in the analyzed specimens.
- The new amorphous binder has demonstrated compressive strength results adequate for the production of concrete. This new concrete would also present some advantages over the OPC concrete: (i) very low heat of hydration release, reducing problems during production of large concrete structures; (ii) no Portlandite is formed upon hydration which may indicate further improved performance in terms of durability, eliminating the problem of Portlandite carbonation due to atmospheric CO_2 that may result in structural damage due to local expansion in the sites were carbonation occurs [8].

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