Strength and Durability of Mortar Using Cork Waste Ash as Cement Replacement

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Cork powder, the major waste from cork processing industries, is generated from grinding, cutting and finishing operations throughout the industrial cork process. Cork powder has been used mainly as fuel in cork industries. Cork waste ash is usually landfilled but if efficiently used in cement based construction materials it could contribute to sustainability. Strength and durability testing was undergone on mortar with 10 and 20% cement replacement with cork waste ash. Although strength is acceptable for 10% cement replacement with cork ash (5% loss at 90 days, compared to control), most durability properties (tested up to 6 months according to test type) reduced performance probably due to a broader pore structure caused by coarse particles in the ash which tested non pozzolanic. Moreover, cork waste ash does not present the necessary requirements in terms of chemical properties considering several standards. Present work has revealed that this cork waste cannot be used as a pozzolan or as a filler in cement based materials. In fact it is known that chemical composition of biomass ash is highly variable due to moisture variations, ash yield and different genetic types of inorganic matter in biomass and therefore it is important to pinpoint which types of biomass waste are adequate or not to use as cement replacement in construction.

Keywords: cork waste ash, sustainability, durability, mortar, concrete

1. Introduction

Cementitious materials, mainly in the form of concrete, are the most successful materials in the world. Every year more than 1m³ is produced per person worldwide. The huge volumes of cement and concrete produced mean that cement production accounts for some 5-8% of man-made CO₂ emissions. Therefore there is increasing pressure to innovate to improve sustainability.

At the same time, public and political awareness on the issue of environmental degradation has intensified. Therefore construction and, in particular, concrete must keep evolving to satisfy the increasing demands of all its users with sustainability as a backing force. Reuse of post-consumer wastes and industrial by-products in concrete is necessary to produce “greener” concrete. Recycling by-products is an environmental-friendly method for large quantities of materials that may otherwise pollute land, water, and air.

Despite the existence of large amounts of industrial waste such as blast furnace slag, fly ash, silica fume, slag and agricultural residues such as rice husk ash, which have been used for many years in large amount as raw materials and components in the cement industry, there are still many other industrial wastes not used yet.

Portugal is the leading producer of cork with 52% of world production. The most important waste from cork processing is “cork powder”, a term used to cover all cork wastes comprising crude cork impurities, cork material powder, cork particles having dimensions lower than permitted for granulates (usually lower than 0.5mm), and sometimes larger pieces. “Cork powder” is produced in all industrial cork processing systems originated in various industrial operations and based on different cork types which are used in the production of multiple cork products. This material has been used mainly as combustion fuel in cork industries, while a small fraction is used as filling agent (mixed with glues) for the worst quality cork stoppers and for linoleum production. It may also be used for example in the manufacture of explosives and agriculture. Cork ash is usually deposited in landfill which is not sustainable. One of the major problems of cork fly ash and cork bottom ash is the effect on environment such as air pollution, due to fineness and groundwater quality, due to possible leaching of metals.

Disposal of solid waste generated from agricultural and industrial production activity is a serious problem and re-use
of such waste materials appears to be a viable solution, not only for pollution, but also for land-filling and high cost of building materials.

The practice of industrial ecology implies that waste products of one industry are recycled as substitutes for raw materials of other industries, thereby reducing environmental impact of both industries.

Cork granules have been studied for application in other industries, namely in the construction industry. In fact, a research study was carried out to use cork granules in lightweight concrete. Results indicated that the addition of cork considerably reduces the density of the composite and enhances failure strain. These properties of the composite are attributed to the cellular structure of cork. Cork presents a low specific weight, great elasticity, flexibility and durability, specific stiffness and strength, impermeability to liquid and gases, resistance to wear and fire, dimensional stability and resistance to reactive agents and microorganisms.

The viability and feasibility of combining waste cork with cementing materials considering fresh and hardened material properties, was also investigated. It could be concluded that the greatest 3 and 7 day cube strengths were achieved by 24 h moisture saturation followed by draining of the cork, prior to use in concrete. Finer cork sizes were most beneficial to achieve optimum mechanical and transport properties. However, high permeability values indicated that concrete-cork composites considered in this study may be vulnerable to poor durability performance.

Authors of the present study were previously involved in research considering use of cork powder in self compacting concrete to replace fine material, which proved to be a successful application of this waste material.

To knowledge of the authors, no research has yet been carried out on cork waste ash as a cement replacement material in cement based composites such as mortar and concrete. The cork industry which supplied cork waste ash for this study produces, on its own, around 800 tons a year of this waste material which has no application so far. Therefore, the aim of this research was to study the potential of using cork waste ash as a partial substitute of cement in mortar so as to assess potential use of this waste in concrete. The study involved a first characterization of cork waste ash including chemical analyses, Scanning Electron Microscopy (SEM) and laser particle size distribution. Then, mechanical and durability properties were assessed, such as alkali-silica reaction resistance (ASR), resistance to chloride ion diffusion and resistance to external sulphate attack. These properties were determined on mortar with different cement replacement dosages as well as for different fineness levels of cork waste ash.

2. Material and Methods

2.1. Materials

Type I 42.5R Portland cement (specific gravity 3.16g/cm³) was used. This cement contains at least 95% Portland cement clinker, therefore the most suitable for this type of study.

Cork waste ash from a Portuguese industry, was dried at 105±5°C for 24 hours. The dried material is henceforward referred to as CPA (Cork waste ash). A finer material, referred to as GCPA (ground cork waste ash) was obtained from CPA submitted to grinding in a planetary mill RETSCH PM 100, using zirconia balls of 1 mm diameter, for 10 minutes at constant 450 rpm.

Particle size distribution and chemical composition of CPA and GCPA are shown in Table 1 and Table 2, respectively.

Pozzolanic activity was assessed by comparing the concentration of calcium ion, expressed as calcium oxide, present in the aqueous solution containing the binder, in this case 90% cement and 10% CPA, after 15 days, with the quantity of calcium ion capable of saturating a solution of the same alkalinity, as described in NP EN 196-510. The binder tests positive for pozzolanicity, if the concentration of calcium ion in the solution is lower than the saturation concentration. Results obtained were a CaO concentration of about 13.6 mmol/l and a OH- concentration of 48 mmol/l, leading to a negative result.

Figure 1 shows Scanning Electron Microscopy (SEM) carried out on cement and CPA/GCPA samples. As can be observed CPA particles are coarser than cement particles. Many particles have a spongy like appearance, possessing a variety of shapes.

2.2. Mortar production

Four mortar types were prepared following the procedure described in NP EN 196-111 a control mix with 100% cement (CTL), two mixes with 10% (CPA 10% and GCPA 10%) cement replacement with cork waste ash (CPA) or ground cork waste ash (GCPA), respectively, and two mixes with 20% (CPA 20% and GCPA 20%) cement replacement with CPA and GCPA, respectively. Mixture proportions are shown in Table 3.

Mortar workability was measured according to ASTM C 10912 and ASTM C 23013, and results are given in Table 3.

2.3. Strength

Flexural and compressive strength testing was undertaken on 40x40 mm x 160mm mortar specimens, following standard procedure in NP EN 196-111 at 28 days for CTL, CPA10 and CPA20 and at 7, 28 and 90 days for CTL, GCPA10 and GCPA20. These 2 studies were conducted separately and results of flexural and compressive strength are presented in Figure 2 and Figure 3, respectively.

2.4. Carbonation

Resistance to carbonation was assessed in accordance with the procedure described in RILEM CPC-1814. Carbonated depth was evaluated on three test specimens for

| Table 1. Particle size distribution of cement, CPA and GCPA. |
|-----------------|----------------|----------------|----------------|
| d(10) µm | d(50) µm | d(90) µm |
|-----------------|----------------|----------------|
| CEM I 42,5 R   | 0.69           | 8.09           | 30.81          |
| CPA             | 10.36          | 31.59          | 71.25          |
| GCPA            | 0.84           | 14.47          | 62.02          |
### Table 2. Chemical and physical properties of cork waste ash and requirements in standards.

| Chemical composition and requirements | Standards |
|--------------------------------------|-----------|
|                                      | GCPA | CPA (%) | NP 4220<sup>25</sup> | NP EN 450-1<sup>26</sup> | ASTM C 618<sup>27</sup> | NP EN 12620<sup>28</sup> |
| SiO<sub>2</sub>                      | 38.15 |          | ≥25%                  |                       |                       |                       |
| Al<sub>2</sub>O<sub>3</sub>          | 3.65  |          |                       |                       |                       |                       |
| Fe total                            | 1.95  |          |                       |                       |                       |                       |
| SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+Fe<sub>2</sub>O<sub>3</sub> | 43.75 |          | ≥70%                  | ≥70%                  |                       |                       |
| CaO                                 | 35.88 |          | ≤2.5% free CaO        | ≤2.5% free CaO        |                       |                       |
| CaO free                            | 10.80 |          | ≤10% Reactive CaO      | ≤25% Reactive CaO     |                       |                       |
|                                      |       |          | or                    |                       |                       |                       |
| MgO                                 | 1.41  |          | ≤4%                   |                       |                       |                       |
| Na<sub>2</sub>O                     | 0.32  |          |                       |                       | ≤5%                   | ≤0.2                  |
| K<sub>2</sub>O                      | 2.13  |          |                       |                       | ≤4%                   |                       |
| Na<sub>2</sub>O<sub>eq</sub>        | 1.72  |          | ≤5%                   | ≤5%                   | ≤4%                   | ≤0.2                  |
| TiO<sub>2</sub>                     | 0.28  |          |                       |                       |                       |                       |
| P<sub>2</sub>O<sub>5</sub>          | 0.87  | 5% (coal fly ash) |                       |                       |                       |                       |
| SO<sub>3</sub>                      | 0.77  | ≤3%      | ≤3%                   | ≤4%                   | ≤0.2                  |                       |
| Cl                                  | Not determined |          | ≤0.1%               | ≤0.1%               |                       |                       |
| LOI                                 | 14.86 | ≤9%      | Category A ≤ 5.0%     | Category B ≤ 7.0%     | Category C ≤ 9.0%     |                       |
| Pozzolanicity                       | Negative |          | Positive            | Positive             |                       |                       |

**Physical properties and requirements**

| GCPA | CPA | NP 4220<sup>25</sup> | NP EN 450-1<sup>26</sup> | ASTM C 618<sup>27</sup> |
|------|-----|-----------------------|--------------------------|--------------------------|
| Specific gravity (g/cm<sup>3</sup>) | 2.601 | By definition |                       |                       |                       |
| Activity Index (%) | 83 | 90 | By definition | ≥ 90% class POZ90/10* (28 days) | ≥ 75% (7 days) |                       |
| (GCPA10 | CPA10) | 73 | 72.5 | (GCPA20 | CPA20) | ≥ 80% class POZ80/20* (28 days) | ≥ 75% (28 days) | ≥ 75% (28 days) |
| Setting time | -- | ≤ (120 min + setting time of cement) | ≤ (120 min + setting time of cement) |                       |                       |
| Final setting time | -- | -- | -- | -- |                       |                       |
| Expansibility | -- | ≤ 10 mm | ≤ 10 mm |                       |                       |

*POZ 90/10. Pozzolanic class identified by the cement/pozzolan ratio which tests positive in the pozzolanicity test according to NP EN 196-5<sup>26</sup>. In this case 90% reference cement and 10% cork waste ash and in the case of POZ 80/20, 80% reference cement and 20% cork waste ash.
Figure 1. SEM photos of cement and CPA.
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Table 3. Mixture proportions and workability of mortars.

| Mixture proportions | Control CTL | Partial cement replacement of |
|---------------------|-------------|-------------------------------|
|                     |             | 10% CPA | 20% CPA | 10% GCPA | 20% GCPA |
| CEM I 42.5 R (g)    | 450         | 405     | 360     | 405      | 360      |
| CPA (g)             | -           | 45      | 90      | -        | -        |
| GCPA (g)            | -           | -       | -       | 45       | 90       |
| Sand (g)            | 1350        | 1350    | 1350    | 1350     | 1350     |
| Water (ml)          | 225         | 225     | 225     | 225      | 225      |
| water/binder        | 0.5         | 0.5     | 0.5     | 0.5      | 0.5      |
| Workability (flow) (mm) | 194±2.9 | 186±0.6 | 185±0.6 | 187±2.4 | 189±4.4 |

Figure 2. Flexural and compressive strength results at 28 days for CPA mortar.

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Each mortar type, water cured at 20°C for the first 14 days followed by 14 days at 20°C and 50% Relative Humidity (RH) and then 90 days in the accelerated carbonation chamber with 5±0.1% carbon dioxide, RH of 60±5% and temperature of 23±3°C. After splitting the specimens, the surface was cleaned and sprayed with a phenolphthalein pH indicator. In the noncarbonated part of the specimen, where the mortar was still highly alkaline, a purple-red colour was obtained. In the carbonated part of the specimen where the alkalinity of mortar is reduced, no coloration occurred. Each value corresponds to the mean of twelve measurements taken around the four sides of the freshly split and sprayed surface of each test specimen. The results can be seen in Figure 4.

2.5. Alkalis silica reaction and SEM observations

In order to measure the ASR expansion for a given mix proportion, an accelerated mortar bar test was carried out on three 25×25×250 mm specimens of in accordance with ASTM C1567.15

Mortar bar specimens were demoulded at 24 hours and then stored in distilled water at 80°C for another 24 hours, after which a zero reading was taken. The bars were then transferred and immersed in 1N NaOH (1 Normal Sodium Hydroxide) solution at 80 °C and periodically measured up to the following 28 days.

Expansion of each mortar bar was measured within 15±5 s after being removed from the 80°C distilled water or alkali storage condition by using a length gauge. Average expansion with time, up to 28 days and average expansion at 14 days of each mortar type are shown in Figures 5 and 6.

Combinations of cement, pozzolanic materials and aggregate that expand more than 0.1% (at 14 days) are indicative of potentially deleterious expansion. However, in the case of indication of deleterious expansion should be confirmed by testing the same combination of materials in concrete.

After testing for ASR, SEM and EDX spectrums were undertaken on GCPA and CTL mortar specimens after 28 days testing as shown in Figure 7 through to Figure 9.

2.6. Chloride ion diffusion

The CTH rapid method is a non-steady-state migration method based on a theoretical relationship between diffusion and migration which enables the calculation of the chloride diffusion coefficient from an accelerated test.16,17

It is based on measuring the depth of colour change of a silver nitrate solution sprayed on specimens previously submitted to a migration test and application of the following Equation 1 and 2.
Where $D_{ns}$ is the apparent diffusion coefficient obtained in a non-steady-state migration test (cm$^2$ s$^{-1}$); $R$ the gas constant $R=8.314$ J (mol K)$^{-1}$; $T$ the absolute temperature (K); $L$ the thickness of specimen (cm); $Z$ the ion valence; $F$ is Faraday constant; $F=9.648 \times 10^4$ J (V mol); $U$ the effective voltage applied (V); $x_d$ the depth of chloride penetration measured by using a colorimetric method (cm); $t$ the time of the test duration (s); $\alpha$ the laboratory constant; $\varepsilon = 0.0764$ if external chloride concentration of 0.5 M; $C_d$ the concentration of free chloride at which the color changes when using the colorimetric method to measure the chloride penetration depth (kg/m$^3$ solution); and $C_0$ is the concentration of free chloride in the external solution.

The procedure for determining the apparent diffusion coefficient ($D_{ns}$) consisted of: after switching off the electrical field the specimens were split in two halves and the penetration of chlorides was measured by using the colorimetric method. This method consists of spraying silver nitrate solution over the split faces, storing them in a dark place for an hour and then exposing them under a fluorescent light for a few hours, after which the average front of the white zone in the central part of each specimen is measured with a precision of 0.5 mm. Apparent diffusion coefficient $D_{ns}$ results are shown in Figure 10.

Test specimens were water cured for 90 days prior to testing.

2.7. External sulphate attack

Resistance to external sulphate attack was evaluated on CTL and CPA10 mortar types according to the Portuguese standard E – 46218, on six (1, 2, 3, 4, 5 and 6) mortar prisms of 20x20x160 mm. Test specimens were immersed in calcium hydroxide solution during 28 days. Then, length was
measured along the 4 side faces of each specimen and taken as the initial readings \((L_0)\). Test specimens 2, 4 and 6 were transferred to a sodium sulphate solution and the remaining specimens were maintained in calcium hydroxide saturated solution. Readings were taken throughout 26 weeks and sulphate solution was renewed every 2 weeks. The actual length increase of each specimen on day \(x\) is taken as:

\[
Exp^{\text{Calc(OH)}_2}(x) = \frac{L_x - L_0}{1600}
\]

\[
Exp^{SO_4,Na_2}(x) = \frac{L_x - L_0}{1600}
\]

\[
Exp^{\text{Calc(OH)}_2} = \frac{Exp(1) + Exp(3) + Exp(5)}{3}
\]

\[
Exp^{SO_4,Na_2} = \frac{Exp(2) + Exp(4) + Exp(6)}{3}
\]

The expansion due to sulphate is:

\[
\text{Expansion (x)} = Exp^{SO_4,Na_2} - Exp^{\text{Calc(OH)}_2}
\]

Expansion along 26 weeks is shown in Figure 11. After testing for external sulphate attack, SEM and EDX spectrums were undertaken on CPA and CTL mortar specimens after 26 weeks testing as shown in Figures 12 to 15.

3. Discussion

3.1. Chemical and physical properties of CPA

As can be seen from Table 2, cork waste ash is mainly composed of silica and calcium oxide of which 11% is free CaO.

Free lime if inter-crystallized with other compounds may only be partially exposed to water before setting\(^{19}\) and thus cause expansion in hardened cementitious composites.
Therefore free lime content should be low which is not the case in this waste material.

Loss on ignition, LOI, presents a high value. However, even higher values, up to 58%, have been reported by other researchers for wood waste ash\textsuperscript{20}. Relatively high LOI in comparison to other type of cement replacement materials namely silica fume and metakaolin may imply a certain degree of inefficiency in the conversion of carbon\textsuperscript{20}. Nevertheless, LOI includes not only carbon content but also any combined water or fixed CO\textsubscript{2} present\textsuperscript{19} usually rendering high water absorption of ash. Moreover it is possible that part of LOI may be attributed to CaCO\textsubscript{3} in the ash which has been found in other types of ash obtained from agro-industrial waste. In fact calcium carbonate was confirmed by XRD in sawdust ash by\textsuperscript{21} and in forest waste ash by\textsuperscript{22}. Poykio et al.\textsuperscript{23} also state that calcium carbonate in a high

Figure 7. SEM on CTL (a) and CPA specimens submitted to ASR (b) and GCPA specimens submitted to 28 day ASR testing (c).
percentage is typically observed in forest waste ash and that although Loss of Ignition is widely attributed to the amount of combustible matter in the sample (especially for coal fly ash), it may not represent rightly the amount of unburnt carbon in ash but rather the volatile fraction. In fact calcium carbonate leads to CaO and CO₂ on heating below 1000°C, the temperature used for determining Loss of Ignition (LOI) in accordance with NP EN 196-2.

Chemical and physical properties of cork waste were compared to requirements in various standards as presented in Table 2. NP 4220 refers to pozzolanic materials in Portugal, NP EN 450-1 to fly ash in Europe which may result from firing of pulverised coal fired simultaneously with co-combustion materials such as vegetable material (like cork waste) and ASTM C 618 refers to coal fly ash or raw or calcined natural pozzolan for use in concrete. As cork
waste ash does not seem to show pozzolanic activity, testing negative for Pozzolanicity, this material was also matched up to filler in accordance with the European standard NP EN 1262028 in terms of chemical properties. However sulphate content surpasses the limit stated in this standard.

As can be seen, properties of cork waste ash fail some of the requirements for each of these standards: The total value of the three oxides SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ is well below the minimum, where demanded, free CaO and LOI overpass limits where stated and, as referred to, pozzolanicity did not test positive, as required in NP 422025.

Through SEM observations (Figure 1), it is shown that cork waste ash is composed of particles with different shapes and sizes. Three main types of particles were observed, diamond shaped, spherical, and spongy like, usually formless. These types of particles proved to be chemically different. Diamond shaped particles seem to be essentially composed of CaO as can be seen in EDS spectrum Z1. Spherical particles, some hollow as in Z2, are also present and of complex composition probably SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO MgO as well as alkalis.

According to Mehta and Monteiro$^{29}$, although most of the particles in fly ash occur as solid spheres of glass, sometimes a small number of hollow spheres called cenospheres may also be present$^{29}$. In the case of fly ash from cork waste this may also be expected.

Spongy like particles, mostly formless, seem to be mainly composed of CaO and MgO. These particles seem abundant and their size relatively greater compared to other CPA particles and also to cement particles, thus confirming particle size distribution presented in Table 1 where it can be seen that CPA is coarser than cement. GCPA is also coarser than cement but grinding CPA to obtain GCPA affected mostly medium and smaller sized particles and less coarser particles, which are probably harder, maybe due to different chemical composition according to size.

Generally, EDS spectrums of the different particles confirmed chemical composition presented in Table 2.

### 3.2. Strength and activity index

Considering flexural and compressive strength, Figure 2 for CPA and Figure 3 for GCPA, it can be seen that cork ash reduces strength and that strength loss is greater with increasing percentage replacement. However at 90 days for GCPA 10% replacement there is a strength loss of only 5% when compared to control and for GCPA 20% replacement, strength loss soars up to 21%, compared to control, as can be seen in Figure 16. This could indicate...
some mild pozzolanic activity although not sufficient to
induce a positive Pozzolanicity test.
In terms of strength and therefore Activity Index, results
(Table 2) generally fail requirements in standards related
to pozzolanic materials. In fact, considering NP 422025, at
28 days, CPA reached the minimum required of 90% for
the Activity Index in POZ 90/10, this is, for 10% cement
replacement with cork waste ash.
However, CPA Activity Index did not attain the required
value of 80% when 20% cement replacement was used, this
is for POZ80/20 class. Strength obtained for GCPA did not
reach adequate values for 10% and 20% cement replacement

Figure 13. EDS on CPA mortar after sulphate attack.
where the Activity Indexes were 83% and 73%, both under the thresholds of 90% and 80%, respectively.

When comparing CPA 10% to GCPA 10%, it is interesting to observe that for this percentage replacement grinding may not be required in terms of strength, lowering production costs.

Unsatisfactory strength results can also be observed in terms of the fly-ash standard where Activity Indexes of 75% and 85% are required at 28 days and 90 days respectively for 25% cement replacement. A replacement level of 20% led to Activity Indexes already below these limits for 28 days (AI=73%, for CPA and GCPA) and 90 days (AI=79% for GCPA) and therefore anticipating even lower values for the required 25% replacement. If ASTM C 618 (2012) is used then strength must be compared at 7 and 28 days with a minimum Activity Index of 75%, disregarding percentage replacement. For GCPA, Activity Index is 85% and 71% for 10% and 20% cement replacement, respectively at 7 days and 83% and 73%, respectively at 28 days. Therefore GCPA used as 10% cement replacement does agree with ASTM C 61827 strength requirements, but not for a 20% cement replacement.

In addition to the cement content reduction, the decrease in strength may be attributed to the increased amount of free water due to reduced amount of material available to react with the water, since cork waste ash is not fully pozzolanic and consists of larger particles and thus lower specific surface reacting – despite the constant w/c ratio used for each mix. The resulting pores in the GCPA or CPA matrixes must be wider compared to the control matrix leading to less dense and more permeable mortar. This will obviously have implications in the durability related properties of cork waste ash mortar.

3.3. Carbonation, alkali silica reaction, chloride diffusion, sulphate attack

Carbonation depth for all blended cement mixtures was greater than for the Portland cement mixture. It was found that carbonation increased along with the increase in GCPA content as expected, due to a more permeable mortar but also to CH reduction. Increasing GCPA replacement results in less cement in the mixture, contributing to CH reduction.

ASR expansion results showed a decreasing expansion in mortar with GCPA compared to CTL.

Increasing the cement dosage replacement by GCPA (10% to 20%) did not affect ASR expansion. Both samples exhibited formation of alkalis-silica gel over deeply grooved surfaces of reactive aggregate. However, cork waste ash content led to slightly lower expansion despite slightly higher alkali content (Na2Oeq of cement = 1.31%). It is possible that gel formed in GCPA mortar was better sustained in the coarser pore system. According to Hobbs30 in concretes containing reactive aggregate which has not shown deleterious expansion due to ASR, gel can often be found filling or partially filling air voids, so that expansion is not observed.

SEM observations were carried out after ASR testing as can be seen in Figures 7, 8 and 9. Gel found on mortar samples, (Figure 8c) Figure 9c)) essentially composed of Si, Ca and Na, appear in the aggregate paste interface. Attacked aggregate presented grooves and gel.

CTH rapid method results show that using GCPA as a partial cement replacement decreases resistance to chloride penetration compared to control mortar especially for 10% replacement. For GCPA 20% the apparent diffusion coefficient was slightly smaller. Incorporation of GCPA, which presents coarser particles compared to cement, led to a more permeable structure.

Sulphate expansion at 26 weeks should be below 0.1% according to the Portuguese standard E-462 and therefore Portland cement used proved not to be sulphate resistant. Incorporating CPA (10%) reduced even further resistance to sulphates. According to Figure 11, CTL and CPA 10% mortar expansion rates were low at the beginning and increased substantially after 10 weeks of immersion in Na2SO4. This result may be explained because as CPA is not fully pozzolanic, portlandite (CH) is available to react with sulphates, promoting the formation of gypsum31.

Regarding SEM and EDS observations, as can be seen in Figure 12 and Figure 13, dispersed plates of gypsum and ettringite were found in CPA mortar.

In case of the CTL mortar, Figure 14 and Figure 15 showed ettringite layers and occasionally structures which seem thaumasite.

For each of the mechanical and durability properties analysed, enhancement due to replacement of Portland cement by GCPA and CPA was calculated by comparing the result with control mortar. A positive result, only observed for ASR expansion, means there was enhancement and a
Figure 15. SEM and EDS on CPA mortar after sulphate attack.

Figure 16. Performance of mortars compared to CTL mortar.
negative result corresponds to a reduction in performance. These results are shown in Figure 16.

### 4. Conclusion

The present study was intended to evaluate use of cork waste ash in cement based materials and the following conclusions can be drawn:

- In terms of physical and chemical characteristics, CPA cannot be considered a pozzolanic-cementitious material according to requirements in ASTM 618\(^{37}\) and fail several requirements in NP EN 450-1\(^{26}\) for fly ash and in the Portuguese standard for pozzolanic materials, NP 4220\(^{35}\). Tested non pozzolanic, CPA cannot be considered as a filler because of high sulphate content;
- Although reasonable strength was obtained for 10% cement replacement with cork waste ash, in terms of durability and as can be seen in Figure 16, cork waste ash reduced performance except for ASR which may be explained by accommodation of gel in the broader pore structure resulting from coarser non-reactive cork waste ash particles.

It has been confirmed that chemical composition of biomass and especially ash components are highly variable due to the extremely high variations of moisture, ash yield, and different genetic types of inorganic matter in biomass\(^{32}\). Therefore it is important to pinpoint which types of biomass waste are adequate or not to use as cement replacement in construction.

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