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MECHANICAL CHARACTERIZATION OF CEMENT PASTES AND MORTARS MADE WITH RECYCLED CERAMIC POWDER

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By

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ABSTRACT

The goal of this thesis is the analyses of the mechanical performance of cement pastes and mortars manufactured with waste ceramic powder.

Waste ceramic materials are really harmful to the environment, and the strategies developed for reducing their disposal to landfill are still at an initial stage. On the other hand, as shown by some researches carried out in the past years, it appears that the majority of this waste, from brick factories, sanitary, electrical insulation, etc., possesses pozzolanic properties activated by baking at high temperatures that the raw clays undergo during the production cycle. Therefore, it is conceivable their re-use as a binder in cementitious materials.

In this report, two powders have been considered: a first one obtained by grinding dental industry waste and a second one from foundry industry. Chemical analysis has been performed and the mechanical performance in bending and compression of pastes and mortars, made with the insertion of this powder as a substitute of the cement or as an additional binder was investigated.

The inelastic volumetric strain caused by the loss of water particles (i.e. shrinkage) of the cement paste was studied as well. The inclusion of these results could incentivize the use of ceramic powder in the concrete mix.

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1

INTRODUCTION

1.1 Cement production

The production of cement starts by heating a mixture of limestone (mainly composed of calcite, CaCO₃) and clays (whose chemical composition is substantially summarized in the formula $x \cdot Al_2O_3 \cdot y \cdot SiO_2 \cdot z \cdot H_2O$, with traces of Fe₂O₃) at high temperatures (up to 1450 ° C), necessary to trigger a chemical recombination process of the reagents. The result is a mixture of tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A), and tetracalcium aluminoferrite (C₄AF), also known as clinker. A 5% by mass of gypsum is then added, whose purpose is to adjust the setting process. The entire mixture is finally ground to the desired particle size.

Aside from this "ordinary" Portland cement composition, cements are also produced containing a small amount of other substances, such as blast furnace slag, fly ash, silica fume, or natural pozzolan, in order to confer to the building material specific properties. Among the typical additions, natural pozzolan presents, in the hydration step, the most similar behavior to the ceramic powder that is going to be investigated in this study.

Natural pozzolans belong to a class of substances based on silica, in which silica is in an amorphous state, found in nature and used as a binding agent since by the ancient Romans. Individually, they lack binding properties, which they acquire in the presence of lime (calcium hydroxide), giving then rise to a secondary hydration as the primary hydration releases molecules of $Ca(OH)_2$. For this reason, concrete containing pozzolan components keeps developing mechanical strength in the long term. Typically the grains of the material have a remarkable fineness and consequently a high specific surface, with lower porosity resulting in the hardened material.

It is also worth remarking that the clinker production process releases into the atmosphere a CO_2 mass almost equal to that of the product: for each ton of clinker, in fact, approximately 850 kg of carbon dioxide are released both in the combustion phase (heating to high temperatures), and in the calcination phase of the material (time period during which the main chemical transformation reactions occur, with production of the related oxides) [5]. Summarizing, the sum of these issues makes the industry of concrete responsible for the emission of 5% of greenhouse gases annually.

1.2 Pozzolanic cement hydration

During cement hydration, the first components to react are the aluminates (C_3A and C_4AF) which in contact with water - and in the presence of gypsum - forming ettringite. This compound, wrapping the clinker grains not yet hydrated, blocks the reaction with water, preventing a sudden loss of workability. If there was no gypsum, the reaction between water and aluminates would end within a few minutes after mixing.

The second stage, called "hardening", involves the silicates: alite (C_3S) and belite (C_2S) hydrate producing C-S-H gel (to which is attributed the mechanical strength of the hardened paste) and Ca (OH)₂. In detail, the C₃S, which reacts faster than the C₂S, forms more Portlandite (Ca (OH)₂) and less gel than the belite.

Calcium hydroxide represents a starting element of the pozzolanic reaction: combined with the silica of the pozzolana and with water, it forms a gel similar to the C-H-S one that increases the mechanical strength of the cement paste, reduces pores, preventing the entrance of chemical agents (chlorides and sulfates, in particular), and enhances the durability. In civil construction applications, it should be noted that pozzolanic cement will take longer time to develop the desired mechanical properties, because the pozzolanic reaction, in order to occur, needs some hydration to produce Ca (OH)₂. On the other hand, the slowness of the reaction restricts excessive differentials in heat release during hydration, limiting the risk of cracks.

The present study will illustrate, through the analysis of laboratory tests (mechanical tests and shrinkage tests), the differences in behaviour between the cement pastes and mortars with the introduction of two different types and percentages of ceramic powder.

1.3 Shrinkage

When a specimen of concrete is exposed to a dry atmosphere, it gradually shrinks; the shrinkage strain is an increasing function of time t which approaches a finite bound at a gradually decreasing rate. Most of the shrinkage of normal concretes is the drying shrinkage, which is caused mainly by increase of capillary tension of pore water and solid surface tension of pore walls, engendered by diffusion of pore water out of the specimen. A part of shrinkage called the autogeneous shrinkage is caused by volume changes associated with the chemical reactions of cement hydration. The autogeneous shrinkage is the only shrinkage that occurs in sealed specimens [17].

2

LITERATURE REVIEW

The cement industry is one of the most active in the world, with an annual output which in 2014 amounted to 4.18 billion tons of material [1], featuring an increase of 2.45% over the previous year and 10.0% over 2012, overcoming some periods of economic slowdown. This industry is particularly active in emerging countries, where the share of production and utilization is 90%, almost half of which is located on the Chinese territory.

At the same time, there is the need for environmental protection, reaffirmed through international summits defining objectives of eco-sustainability to be achieved through the reduction of harmful emissions, the reduction of waste generation, planning new recycling strategies with the aim of rehabilitating materials once considered waste for new use, and creating a suitable mechanism to reduce the burden mining, industrial, and energy supply.

Detailed analysis on the composition of the waste showed that the majority of waste material produced by human activity is linked to Construction and Demolition (C & D), with an incidence compared with global production of around 75% [2] where the highest percentage of it (approximately 54%) consists of ceramic materials (bricks, tiles, electrical insulators, health, etc.). Still, ceramic waste is discarded from the production process for not meeting the quality standards; the percentage of such re-utilizable waste is around 2% of the mass produced for technologically advanced industries [3].

With reference to these materials, many researches have now shown their suitability as a raw material for the production of cement clinker, without the final product being significantly altered from a chemical and mechanical point of view. Indeed, modest doses of ceramic content seem to improve the mechanical performance and durability. Studies have reported that waste ceramic materials may become a cheaper but almost equivalent alternative to metakaolin or ground granulated blast furnace slag, fly ash and other materials as supplementary binder in concrete.

Nowadays, the regulations in most of the world countries prescribe landfill disposal for this kind of waste - which presents a good resistance to atmospheric, chemical, and biological agents. This generates at production factories (where most of the landfills are located to avoid transport costs) excessive environmental pressure with risk of air and soil pollution.

As an example, the case of India can be cited [4]: in 2013 the average annual production of ceramics was 100 million tons, of which an amount between 15% and 30% constituted waste material at the end of the industrial cycle, and was abandoned in the open spaces next to the factories or in illegal underground deposits despite specific areas for their disposal had been previously identified by the territorial administrations. Any recycling activitiy was not considered because it had not yet been regulated.

In parallel, the cost of a kilogram of this residue was equal to 0.20 Rupees, against 6.40 Rupees paid for each kilogram of cement: it is evident that, in addition to being eco-friendly, the re-use of such waste is advantageous also from the economic point of view. For a standard concrete mix, in fact, the cost of the concrete can be reduced up to 12.67% by replacing 30% of the cement with ceramic powder.

A significant amount of research activities has been carried out with reference to the reuse of ceramic waste from the demolition or construction-related industries, confirming the possibility of its re-utilization for the production of blended cements, or as aggregates (both fine and coarse) for concrete, improving mechanical strength and durability. In the following survey, we will focus on the use of ceramic waste from dental and foundry industries, after being crushed and pulverized, as partial replacement of cement. Reference mixtures containing only cement have been prepared, and mixtures with replacement ratios of 10% and 30% by volume, both varying the water / cement ratio and keeping it constant.

In [4, 10] it is highlighted as mixtures with a higher ratio of substitution cannot reach the minimum threshold of resistance to compression at 28 days resulting into a structural risk, if they were to be employed. In particular, in [10] the maximum limit for the replacement ratio is fixed at around 35%.

Also a research performed by some Czech scholars [3] mentioned a substantial constancy of mechanical properties up to 20% in the replacement ratio, while noted huge losses in mixtures with 40 and 60% of ceramic powder.

In 2009, a similar research to this one was conducted by a Japanese team, led by Professor Hiroshi Higashiyama [12], on compressive strength and resistance to chloride ion penetration of mortars made employing ceramic waste as fine aggregate. The ceramic waste from electrical insulators provided by an electric power company in Japan was crushed and ground to produce fine aggregates for mortars. The data obtained seem to confirm that all mixtures, except a mortar with substitution ratio of 30 %, at the seventh day of curing had higher resistance values than the reference one. A marked increase in mechanical strength was already achieved by simply replacing the fine aggregate (sand fluvial) by shattered pottery. In the long term, the mortars prepared with additions of ceramic powder with substitution ratio of 30% (containing ceramic aggregate) reached the highest strength values. Furthermore, the use of ceramic materials gave an improvement to the mortar in terms of reduction in volume of the pores and their diameter, and the protection from the penetration risk of chloride ions, both important parameters for the material durability.

Even more interesting researches have studied the combined action of various particle sizes of the ceramic waste. This would lead to even more advantageous solutions from the environmental and economic point of view. For example in [14], internal curing with porous ceramic waste aggregate (PCA) for portland blast furnace cement type B concretes (BB) is effective in decreasing pore volume when BB is exposed to drying at an early age.

The performance advantages of the re-use of ceramic waste in form of aggregates do not stop here: in [13], in fact, it has been shown that the use of the ceramic waste as coarse aggregates in the production of concrete is beneficial: the mixture is much more workable, because of lower water absorption and higher surface smoothness of the ceramic aggregate. Moreover, the ceramic aggregate also has greater resistance to chemical attack: in the soundness test, the ceramic samples show a conservation of mass far higher than that of the aggregates currently in circulation and stemming from the fragmentation of calcareous rocks. The mechanical performance suffers an unnoticeable reduction, not such as to affect its use in ordinary works and that could also be neglected by the combined action of the ceramic powder. The hardened mixture, however, had a lower Young's modulus with a decrease of about 3GPa with respect to values of about 20GPa. It is not of secondary importance the fact that the aggregate arising from crushed ceramic waste has lower density (about 150 to 200 kg / m3, [15]) than that of the common rock aggregate: the same mechanical performance can thus be obtained with lighter structural elements. The ceramic waste materials, again because of their consistency and chemical stability, also provide effective shielding to the deposits of radioactive wastes: their low porosity and their inactivity reduce the risk of filtration of pollutants in the subsoil [2].

It is also necessary to be careful in controlling the ceramic powder used as raw material. Because, according to the origin, it could be a source of pollution itself. For example, the enamel surface of the ceramic waste used in [11] for the production of cement clinker contained potentially toxic substances (specifically, oxides of zinc, boron, and zirconium), which could be, however, retained by the cement matrix (in the case of zirconium), or could leach into the environment (zinc and boron), even if without reaching the concentrations threshold recognized as dangerous. However, before launching a massive industrial production, it is good to perform all the chemicals analysis necessary to dispel possible environmental threats.

The aforementioned researches on reuse of ceramic waste of aggregates form in concrete ([13], [14], [15]) would seem to attest that limited additions of ceramic aggregates do not compromise the durability of the mix. This would therefore lead to

hope that similar results could be obtained also with regards to the introduction of ceramics as a binder.

3 EXPERIMENTAL ACTIVITY

The characterization of the mechanical behavior of mixtures containing ceramic powder has been accomplished through the production of cement pastes and mortars with different levels of ceramic powder and two different types of ceramic powder, by performing bending and compression tests at different ages: 1, 3, 7, 28, 56, and 84 days. In the case of cement mortars, it was also investigated the workability through minislump tests.

To this purpose, two set of specimens were produced: a standard set with substitution ratios of the cement by 10% and 30% (PCEM10, PCEM30 and MCEM10, MCEM30); and another set with w / c ratio constant and cement replacement rate of 30% (PAC-CONST30 and MAC-CONST30). For both paste and mortar also reference specimens with only cement were cast (PCEM-REF and MCEM-REF).

The shrinkage behaviour of the cement pastes and mortars with ceramic substitution was also studied considering the same sets of specimens.

In the set of specimens obtained with simple volumetric replacement of cement with the ceramic powder there is an increase in the water / cement ratio compared to the initial value, which may lead to resistance losses also in the short term, before the ceramic may manifest any pozzolanic property.

3.1 Materials employed

3.1.1 Ceramic powder

The first ceramic powder has been obtained by crushing wastes from the production process of dentures, where it is used both individually and in combination with metals (generally titanium, chromium-nickel, cobalt-chromium, gold, or platinum). In Figure 1, an example of a dental prosthesis can be observed. The "dental porcelain" used in this area have a chemical composition with a high content of feldspar (75 Fig. 1 \pm 85%), followed by quartz (12 \pm 22%) and



Fig. 1 – Example of dental prosthesis

various oxides (among which stands the boron oxide), regulated by the ISO 4824 [6]. Kaolin is almost absent (regulations up to 4% the maximum possible concentration) for aesthetic reasons, whereas in the construction industry it is widely used for the production of bricks and other ceramic materials thanks to allow the workability enhancement it can give to the mixture. Distributed in dust, these "porcelain" (more properly considered ceramics or feldspathic glasses) are mixed with water and possibly other substances (rubber, starch, etc.) to then be cooked at temperatures between 800 $^\circ$ C and 1400 ° C, causing the sintering (i.e., the formation of a vitreous paste) of the granular particles. As It can be noted in other research articles [2, 3], temperatures between $600 \div 900$ ° C lead to the elimination of water of crystallization and the consequent alteration of the molecular structure of the ceramic, with transition from a crystalline morphology to an amorphous alumino-silica, and separation of inert and reactive aluminum oxide. It is precisely this new spatial distribution of the molecules, characterized by high disorder, which confers reactivity to the ceramic material, activating the already mentioned pozzolanic properties. Afterwards the material is finely ground to increase the specific surface area and, therefore, improve the speed and quality of the hydration reactions, as well as the mechanical strength of the hardened paste and the characterization of its pores.

[15] The second ceramic powder comes from foundry industry, which frequently needs ceramic parts with different geometries for contact with metallic alloys. These parts must have mechanical strength, resistance to the erosive wear and chemical attack of the liquid metal, high refractoriness and thermal insulation. Considering these factors, INEGI (Institute of Mechanical Engineering and Industrial Management) has been developing a manufacturing process, which allows rapid manufacturing of ceramic prototypes and pre-series, with different shapes, controlled levels of porosity and adequate resistance in contact with liquid metals. Although the existence of porosity in the parts is responsible for a significant decrease in the mechanical properties, it gives them the possibility to exhibit thermal insulation and low dimensional variation (6% maximum during all the manufacturing cycle), which makes this process extremely interesting for applications related with the foundry industry.

After the mould manufacturing, ceramic slurry is poured into the mould. Different ceramic materials (molochite, zircon and titania), a binder (hydrolysed tetraethoxysilane) and a catalyst (ammonium hydroxide) compose the slurry. After a short period of time, controlled by the catalyst amount and the room temperature, the ceramic part obtained is demoulded and burned (stabilised). The green ceramic part is then sintered to increase the mechanical strength.

Ceramic crucibles for melting metallic alloys can be obtained with different ceramic slurries compositions. These ceramic parts have very low green mechanical strength (around 2 MPa) and exhibit porosity levels around 50%. Previous work demonstrated that a slurry composed by 60 % zirconium silicate, 30 % aluminosilicates and 10 % titanium, was the most suitable (lower porosity level and roughness and easier processing) for this type of application. Considering this, only this slurry was tested.

[7] As a matter of fact the pozzolanic activity index of a ceramic powder is not simply a function of the greater or lesser fineness of its grains, but also of its particle size distribution: a more homogeneous material (in the limit, single grain size) in fact shows greater reactivity and produces better results than an identical material with scattered distribution.

All reported values with reference to the particle size of the first and the second ceramic are in the following tables and graphs:

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
0.100 0.110 0.122 0.135	0.00 0.00 0.00	0.800 0.884 0.976 1.077	3.48 3.65 3.80	6.404 7.070 7.806 8.619	1.33 1.14 0.95	51.245 56.580 62.470 68.973	0.11 0.09 0.05	410.077 452.768 499.903 551.945	0.00 0.00 0.00
0.135 0.149 0.164 0.201 0.221 0.244 0.269 0.297 0.328 0.362 0.400 0.442 0.488 0.538 0.595 0.655 0.735	0.00 0.00 0.00 0.11 0.34 0.49 0.66 0.86 1.11 1.41 1.71 2.29 2.56 2.82 2.56 2.82 3.06	1.077 1.189 1.313 1.450 1.601 1.767 1.951 2.154 2.379 2.626 2.900 3.202 3.535 3.903 4.309 4.758 5.253	3.91 3.98 4.03 4.00 3.92 3.81 3.67 3.50 3.30 2.86 2.63 2.40 2.17 1.95 1.74	8.619 9.516 10.507 11.601 12.809 14.142 15.614 17.240 19.035 21.016 23.204 25.620 28.287 31.232 34.483 38.073 42.037	0.77 0.60 0.45 0.32 0.20 0.11 0.05 0.01 0.00 0.00 0.00 0.00 0.0	68.973 76.154 84.081 92.835 102.499 113.170 124.952 137.960 152.322 168.179 185.688 205.019 226.362 249.927 275.946 304.673 336.391	0.04 0.03 0.02 0.03 0.08 0.16 0.26 0.36 0.45 0.51 0.50 0.48 0.30 0.01 0.00 0.00	551.945 609.406 672.848 742.894 820.233 995.623 999.903 1103.998 1218.929 1345.826 1485.933 1640.625 1811.422 2000.000	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0
0.800	3.28	6.404	1.54	51.245	0.11	410.077	0.00		

Table 1 – Granulometric data results for the first ceramic powder.

Mesh No	Aperture µm	Volume In %	Vol Below %	Mesh No	Aperture µm	Volume In %	Vol Below %	Mesh No	Aperture µm	Volume In %	Vol Below %
10	2000	0.00	100.00	35	500	0.00	100.00	120	125	0.10	96.97
12	1700	0.00	100.00	40	425	0.00	100.00	140	106	0.10	96.86
14	1400	0.00	100.00	45	355	0.00	100.00	170	90	0.04	96.83
16	1180	0.00	100.00	50	300	0.00	100.00	200	75	0.06	96.77
18	1000	0.00	100.00	60	250	0.31	99.69	230	63	0.08	96.69
20	850	0.00	100.00	70	212	0.81	98.88	270	53	0.16	96.53
25	710	0.00	100.00	80	180	0.83	98.04	325	45	0.18	96.35
30	600	0.00	100.00	100	150	0.71	97.33	400	38	0.15	96.20
35	500	0.00	100.00	120	125	0.37	96.97				00.20

Table 2 – Sieves data results for the first ceramic powder.



Graph 1 – Granulometric data results for the first ceramic powder.



Graph 2 – Sieves data results for the first ceramic powder.

Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %	Size (µm)	Volume In %
Size (μm) 0.100 0.110 0.122 0.135 0.149	Volume In % 0.00 0.00 0.00 0.00 0.00	Size (μm) 0.800 0.884 0.976 1.077 1.189	Votume In % 0.00 0.00 0.00 0.00 0.00	Size (μm) 6.404 7.070 7.806 8.619 9.516	Volume In % 0.13 0.13 0.13 0.13 0.13	Size (µm) 51.245 56.580 62.470 68.973 76.154	Volume In % 0.52 0.65 0.74 0.84	Size (μm) 410.077 452.768 499.903 551.945 609.406	Volume In % 2.80 3.42 4.08 4.71 5.27
0.164 0.181 0.200 0.221 0.244 0.269 0.297 0.328 0.362 0.400 0.442 0.488 0.538 0.595 0.656 0.725 0.800	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	1.313 1.450 1.601 1.767 1.951 2.154 2.379 2.626 2.900 3.202 3.535 3.903 4.309 4.758 5.253 5.800 6.404	0.00 0.01 0.02 0.01 0.11 0.12 0.13	10.507 11.601 12.809 14.142 15.614 17.240 19.035 21.016 23.204 25.620 28.287 31.232 34.483 38.073 42.037 46.413 51.245	0.14 0.15 0.16 0.18 0.20 0.23 0.26 0.28 0.31 0.34 0.34 0.36 0.38 0.40 0.42 0.44 0.48	84.081 92.835 102.499 113.170 124.952 137.960 152.322 168.179 185.688 205.019 226.362 249.927 275.946 304.673 336.391 371.411 410.077	0.96 1.08 1.19 1.28 1.34 1.37 1.36 1.32 1.26 1.19 1.16 1.17 1.27 1.48 1.80 2.25	672.848 742.894 820.233 999.903 1103.998 1218.929 1345.826 1485.933 1640.625 1811.422 2000.000	5.71 5.98 6.06 5.94 5.63 5.14 4.51 3.78 2.98 1.98 1.25

Table 3 – Granulometric data results for the second ceramic powder.

Mesh No	Aperture µm	Volume In %	Vol Below %	Mesh No	Aperture µm	Volume In %	Vol Below %	Mesh No	Aperture µm	Volume In %	Vol Below %
10	2000	2.40	100.00	35	500	E 00	36.98	120	125	2.09	13.77
12	1700	2.40	97.60	40	425	0.20	31.70	140	106	2.00	11.69
14	1400	6.00	91.60	45	355	4.06	27.64	170	90	1.78	9.91
16	1180	7.72	83.87	50	300	2.62	25.01	200	75	1.61	8.30
18	1000	9.14	74.73	60	250	2.24	22.78	230	63	1.21	7.09
20	850	9.82	64.91	70	212	1.94	20.83	270	53	0.97	6.11
25	710	10.82	54.08	80	180	2.08	18.76	325	45	0.79	5.33
30	600	9.11	44.98	100	150	2.49	16.27	400	38	0.73	4.59
35	500	8.00	36.98	120	125	2.50	13.77				

Table 4 – Sieves data results for the second ceramic powder.



Graph 3 – Granulometric data results for the second ceramic powder.



Graph 4 – Sieves data results for the second ceramic powder.

The first ceramic powder used for the production of test specimens presents a whitish color, with high fineness than that of the cement while the second ceramic powder is darker and coarser than the cement.

3.1.2 Cement

For the production of test specimens, cement CEM I 52.5R was used produced by the Italian company Italcementi. It is, as per UNI EN 197-1, a material almost exclusively made of clinker ($95\% \div 100\%$), with calcium sulphate content (gypsum) lower than 4%, and chloride content lower than 0.10%. It is also capable of developing a compressive strength of 30,0MPa after two days and quick-setting ("R" in abbreviation), which means that the paste starts setting after 45 minutes from casting causing also a considerable heat of hydration release.

3.1.3 Fine aggregate

For the production of mortars, it is used quartz sand provided by Cave Rocca and commonly used in building works, sieved three times to select a particle size not larger than 4 millimeters.

3.1.4 Superplasticizer

To make a workable mixture with low water / cement ratios, plasticizers are used (or superplasticizers if the reduction of water without altering the final characteristics of the mixture exceeds 12% by volume). These are polymer-based substances which space mutually the grains constituting the binder facilitating the mutual sliding and increasing fluidity. In our case, the superplasticizer Glenium ACE 30 has been used provided by BASF-SE. According to the requirements, the admixture must be added when the mixture already contains 80 \div 90% of the total mixing water, so that its effectiveness is maximum, and at a temperature comprised between 15 and 20 ° C. This admixture also accelerates the setting time and thus the release of the heat of hydration.

3.1.5 Water

Common tap water has been used. Some researches show the possibility of using some types of drainage water, as long as it does not contain excessive concentrations of specific pollutants that may be a risk of chemical attack for concrete.

3.2 Description of the mixture

To get the reference mixtures (series without substitutions in the binder) we proceed to the transformation, by volumetric equivalences, of the dosage of the different components of a concrete mix design prepared by Banagher Precast Concrete Ltd. (See table 5), and submitted by Irish colleagues together with the ceramic powder used. In these transformations, the filler (Betocarb lime) has been assimilated to the cement; the gravel content of the initial mixture has been also ignored. All doses were then identified by means of simple proportions, with the aim of giviving a volume of 1.2 liters of mixture for the cement paste, and 1.5 liters for the mortar: the excess of 0.3 liters is used to perform the workability tests with a mini-cone. An example of mix

design calculations is shown on page 11. Secondly, the cement has been replaced by ceramic powder, always on a volumetric basis, by removing the first one in percentages of 10% and 30%, and introducing the second one considering a ceramic powder density of 2000 kg/m³. This results into a variation of the water/cement ratio (in mass and volume) with respect to the standard mixture, but the volumetric ratio between water and total powder is kept. A second set of specimens has then been cast made without changes regarding the w / c ratio, with cement to ceramic replacement rate of 30%. All this procedure is carried out twice, once for each type of ceramic powder.



Banagher Precast Concrete Limited,

Quality Assurance.

CONCRETE MIX DESIGN

MIX DESIGN NAME:	C50/60 SCC Mix
MIX DESIGN CODE/CLASSIFICATION:	REC NO. 986/CEM I
PRODUCTION LOCATION:	Banagher Precast Concrete Plant.

MATERIAL DESCRIPTION	MASS	MASS PER M3		MATERIAL SUPPLIER / COMMENTS
Cement Type – Rapid Hardening Portland Cement CEM I	400	CEMI	Kgʻs	Irish Cement.
GGBS	0		Kgʻs	Irish Cement.
Betocarb Lime	14	40	Kgʻs	Omya Ltd.
20mm Aggregate	(0	Kgʻs	Banagher Precast Concrete Ltd.
14mm Aggregate	3	90	Kgʻs	Banagher Precast Concrete Ltd.
8mm Aggregate	4	50	Kgʻs	Banagher Precast Concrete Ltd.
Sand	780		Kgʻs	Banagher Precast Concrete Ltd.
Crushed Limestone Fines	0		Kgʻs	Banagher Precast Concrete Ltd.
Max Free Water	160		Ltrs.	
Water/Cement Ratio	0	.4	Ratio	
ADMIXTURE DESCRIPTION				
Glenium Ace 474		-	Ltrs.	B.A.S.F
Premia 360	4	.6	Ltrs.	Chryso
Sika Rapid 2		-	Ltrs.	Sika
Excel 650		-	Ltrs.	Chryso
Sika Premier		-	Ltrs.	Sika
Mastermatrix 233		-	Ltrs.	B.A.S.F
Sika Rapid 2 Excel 650 Sika Premier Mastermatrix 233		- - -	Ltrs. Ltrs. Ltrs. Ltrs.	Sika Chryso Sika B.A.S.F

Note 1:	The type and quantity or requirements.	of admixtures may vary depending on se	asonal conditions and production de-moulding
REV: 0		ISSUED BY:B O' Meara	DATE: 28/07/15



3.2.1 Example: PCEM-REF

Volumetric quantities of the mixture delivered from the *Banagher Precast* Concrete:

	Initial quantities of the mixture										
Ceramic	Cement	Filler	Water	Plasticizer	Sand	Gravel					
2000	3100	2600	1000	1055	2600	2600	[kg/m ³]				
-	400	140	160	4.853	780	840	[kg]				
-	0.1290	0.0538	0.1600	0.0046	0.3000	0.3231	[m ³]				

Table 0 – Initial quantities of the mixtur	ıble 6 – Initial quantities	of the	mixtur
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For the cement paste only the sum of the cement volume (fillers equated to cement), water and plasticizer was taken into account. Then the dosages (0.0012m3) were scaled to the required casting volume:

$$V_f = \frac{V_i}{V_{tot,i}} V_{tot,f} \qquad (1)$$

The following results were obtained:

	Transformed quantities of the mixture											
Ceramic	Cement	Water	Plasticizer	Sand	Gravel							
0	0.632	0.553	0.016	-	-	[1]						
0	1958	553	17	-	-	[g]						

Table 7 – Transformed quantities of the mixture

3.2.2 Other mixtures

Subsequently was substituted the cement by ceramic powder, removing 10% and 30% of it on a volumetric basis and replacing it by the powder. The final mixtures for the cement pastes are the following:

	Table of cement pastes											
	Ceramic	Cement	Water	Plasticizer	Sand							
PCEM-REF	0	1958	553	17	-	[g]						
PCEM10	126	1762	553	17	-	[g]						
PCEM30	379	1370	553	17	-	[g]						

Table 8 – Table of cement pastes

For the composition of the MCEM-REF mortar a similar procedure has been followed, taking care to introduce in the denominator of the equation (1) also the sand volume. The final volume of the mixture obtained at the end is equal to 1.5 liters, for the execution of the workability tests. The dosages thus obtained are the following:

Table of cement mortars										
	Ceramic Cement Water Plasticizer San									
MCEM-REF	0	1313	371	11	1807	[g]				
MCEM10	85	1182	371	11	1807	[g]				
MCEM30	254	919	371	11	1807	[g]				

Table 9 – Cement mortars

The following table (the same for both cement pastes and cement mortars) shows how the ratio between water and cement is varied in the different investigated mixes.

Variation w/c ratio						
	w/c					
P/M-REF	0.282					
P/M10	0.314					
P/M30	0.403					

Table 10 – Variation w/c ratio

In order to obtain the correct dosages of the constituents of the PAC-CONST30 was sufficient to express the volumes of the different constituents as a function of the volume of cement in the final mixture, thus obtaining the final volume of cement and consequently all the other volumes as shown:

Table cement paste constant w/c ratio									
	Ceramic Cement Water Plasticizer								
PAC-CONST30	0.220	0.513	0.449	0.026	-	[1]			
	440	1590	449	28	_	[g]			

Table 11 – Cement paste constant w/c ratio

Regarding the cement mortars with constant water / cement ratio, the final composition is shown in table 12:

Table cement mortar constant w/c ratio										
	Ceramic	Sand								
MAC-CONST30	0.143	0.333	0.291	0.038	0.695	[1]				
	285	1033	291	40	1807	[g]				

Table 12 - Cement mortar constant w/c ratio

In summary, the blends design are the following (figures in grams):

Summary table of the mixtures										
	PCEM REF	PCEM 10	PCEM 30	MCEM REF	MCEM 10	MCEM 30	PAC CONST30	MAC CONST30		
Ceramic	-	126	379	-	85	254	440	285		
Cement	1958	1762	1370	1313	1182	919	1590	1033		
Water	553	553	553	371	371	371	449	291		
Plasticizer	17	17	17	11	11	11	28	40		
Sand	-	-	-	1807	1807	1807	-	1807		

Table 13 – Summary table of the mixtures

3.3 Preparation of test specimens

For each mixture three specimens 40x40x160 mm3 (Fig. 3) were cast, in accordance with European Standards [9]. The mixture was prepared with the apparatus Mixer L5, from Controls Italy (Figure 4). The demolding of the formwork was performed after one day curing in an environment at 95% RH, in which the demolded specimens were also cured until the age of testing.

In detail, each specimen was prepared according to the following procedure in an environment at 65% RH:

- The different constituents were weighed in dry conditions;
- The powders were mixed in dry conditions (cement, ceramic, sand) for one minute (this phase was skipped in the case of PCEM-REF);
- 75% of the mixing water was added along a time interval of 30 seconds, after which mixing was continued for a minute and a half;
- Superplasticizer and the remaining part of water were then added, and mixing was then continued for other five minutes.



Fig. 3 - Hardened specimens

At the end, the fluid mixture was cast in metal molds slightly lubricated with oil to facilitate the future demoulding, covering them with a glass panel without completely occlude the formwork. In such a way the air bubbles, which may develop, did not remain entrapped on the specimens' surface. Simultaneously, the mini slump-flow tests were performed in the case of mortars. Given the fluidity of the mixtures, there was no need for any vibration.

Pertaining to the shrinkage test, each aforementioned sample was mixed with the same process described for the mechanical tests. However they are cast in such a way, that a protruding metallic pin will be fixed to each extreme of the concrete prism. For the first 24 hours the specimens were kept in a 95% relative humidity environment. Next, the specimens were removed from the mold and taken to a 50% relative humidity chamber. The samples were kept in this environment at every time and are measured daily for the first 28 days and then they are measured weekly. In order to measure autogenous shrinkage specimens are wrapped in aluminium foils.



Fig. 4 - Mixer

3.4 Mechanical tests

At different stages of aging, bending and compression tests were performed according to EN196.

The tests were performed with instrumentation from the company "Comazzi Oscar", PF10,25 model (Figure 5).



Fig 5 – Machine for mechanical tests

For the determination of the flexure strength, three point bending tests were performed as per (Fig. 6). The value of the resistance, expressed in MPa, is given by the following formula:

$$R_f = \frac{1.5 * F_f * l}{b^3}$$
(2)

with F_f indicating the ultimate load in Newtons, l the distance between the load application points, and b the length of the side of the section of the specimen. The values of l and b, in our case, are equal to 106,7mm and 40mm.

The compressive strength test (Fig. 7) was instead carried out on the two halves resulting from the specimen breakage, and the strength is determined by the basic formula:

$$R_c = \frac{F_c}{1600} \tag{3}$$

being 1600(mm2) the surface of the loading plate, with square shape, and F_c the applied load.



Fig. 6 – Specimen subjected to bending



Fig 7 - Specimen subjected to compression

3.5 Shrinkage test

In order to perform this test, three 40 x 40 x 160 mm specimens were produced for each mixture considered for the mechanical test (PCEM10, PCEM30, MCEM10, MCEM30, PAC-CONST30, and MAC-CONST30 for each type of ceramic; as well as PCEM-REF and MCEM-REF for reference purposes). The measurement of the evolution of the specimen's shortening, i.e. shrinkage strain, was measured with a strain gauge with a 0.001 mm precision. One of the aforementioned specimens was sealed after it is removed from the mold in order to measure the autogenous shrinkage, additionally the unsealed specimen will be used to measure the total shrinkage. It is worth remarking that on this work the axial deformation will be presented even though shrinkage is a volumetric strain.



Fig. 8 – Strain Gauge and concrete specimen

When the specimens were taken to the 50% relative humidity room, they were measured with the strain gauge. This measurement (plus the original 160 mm) was taken as the original length (L_0) of each sample. For the first 28 days the variation of the length has been measured daily (ΔL) and measured weekly afterwards. The corresponding shrinkage strain was then calculated with the following formula:

$$\xi_{sh} = \frac{\Delta L}{L_0} \tag{4}$$

3.6 Workability test

The workability tests were performed only for the mortars, due to the excessive fluidity of the cement pastes. Tests were performed according to (UNI EN 1015-3), a mini-cone with a capacity of about 0.35 liters, whose dimensions are summarized in Figure 9.

In figure 10 and 11 some snapshots of the test procedure are shown.



Fig.9 – Cone for the slump-flow test



Fig. 10 – Lifting phase



Fig. 11 – Final configuration of the slump test

4

RESULTS AND COMMENTS

4.1 Workability and mixture appearance

At the end of mixing, all the cement pastes showed a markedly liquid appearance. There were no significant differences between the paste prepared with only cement and those made with partial replacement of the ceramic powder for both types of ceramic powder.

With reference to the mortars in Table 14 and 15 the results are reported of workability tests of the various mixtures. Quite often they have been obtained equivalent measures in the two directions, that of the maximum length and the orthogonal one. From the data it is clear that the presence of ceramic powder slightly increases the workability of the mix for both types of ceramic powder. This may be due to two factors: on the one hand, the ceramic powder is initially inert because the pozzolanic reaction takes longer times; on the other hand, in the case of the second ceramic powder the lesser fineness also means a lower specific surface area, which is reflected in a lower subtraction of water for the absorption phenomenon.

However, this small increase in workability seems to stop from an addition of 10% of ceramic powder even for the second ceramic powder workability decreases slightly from 10% to 30% of cement replacement.

Results of the slump-flow test (cm)									
Days	MCEM	-REF	MCEN	/10	MCEN	/130	MAC-COI	NST 30	
	24		34,5		33,5		30		
	24		33,5		33		29,	5	
1	Average	24	Average	34	Average	33,25	Average	29,75	
	Standard deviation	0	Standard deviation	0,25	Standard deviation	0,0625	Standard deviation	0,0625	
	28		36,	5	35		30		
	28		35		33		29		
3	Average	28	Average	35,75	Average	34	Average	29,5	
	Standard deviation	0	Standard deviation	0,5625	Standard deviation	1	Standard deviation	0,25	
	28,5		34		32		28		
	28		34		31		28		
7	Average	28,25	Average	34	Average	31,5	Average	28	
	Standard deviation	0,0625	Standard deviation	0	Standard deviation	0,25	Standard deviation	0	
	33		32		33		31		
	33		31,5		32,5		31		
28	Average	33	Average	31,75	Average	32,75	Average	31	
	Standard deviation	0	Standard deviation	0,0625	Standard deviation	0,0625	Standard deviation	0	
	32		34		32		30		
	32		33		31		29,5		
56	Average	32	Average	33,5	Average	31,5	Average	29,75	
	Standard deviation	0	Standard deviation	0,25	Standard deviation	0,25	Standard deviation	0,0625	
	34		30,	5	31		29		
	34		31,	5	30		31		
84	Average	34	Average	31	Average	30,5	Average	30	
	Standard deviation	0	Standard deviation	0,25	Standard deviation	0,25	Standard deviation	1	

Table 14 - Slump-flow test results for the first ceramic (cm)

Results of the slump-flow test (cm)										
Days	MCEM-	REF	MCEM	10	MCEM	30	MAC-CON	ST 30		
	34		32		31,5		31			
	36		33		32,5	6	32,5			
1	Average	35	Average	32,5	Average	32	Average	31,75		
	Standard deviation	1	Standard deviation	0,25	Standard deviation	0,25	Standard deviation	0,5625		
	35		32		28		30			
	35		32,5		27,5		30,5	-		
3	Average	35	Average	32,25	Average	27,75	Average	30,25		
	Standard deviation	0	Standard deviation	0,0625	Standard deviation	0,0625	Standard deviation	0,0625		
	27		34		32,5		31,5			
	27		34		33		32			
7	Average	27	Average	34	Average	32,75	Average	31,75		
	Standard deviation	0	Standard deviation	0	Standard deviation	0,0625	Standard deviation	0,0625		
	22		32		33		29,5			
	22		32		34,5		30			
28	Average	22	Average	32	Average	33,75	Average	29,75		
	Standard deviation	0	Standard deviation	0	Standard deviation	0,5625	Standard deviation	0,0625		
	22		32,5		28,5		31			
	22		33		29,5		31			
56	Average	22	Average	32,75	Average	29	Average	31		
	Standard deviation	0	Standard deviation	0,0625	Standard deviation	0,25	Standard deviation	0		
	30		35		28		32,5			
	30,5		34		28		31,5			
84	Average	30,25	Average	34,5	Average	28	Average	32		
	Standard deviation	0,062 5	Standard deviation	0,25	Standard deviation	0	Standard deviation	0,25		

Table 15 - Slump-flow test results for the second ceramic (cm)

4.2 Results of compression test

Compression tests were performed on the two halves resulting from the breakage of specimens employed for flexural tests.

All recorded compressive strength values are reported in Table 16 and 17.

It is possible to obtain a quick overview of the results through the bar graphs (Graphs 12, 13, 14 and 15).



Graph 5 – Compression strength cement pastes. First ceramic powder



Graph 6 – Compression strength cement pastes. Second ceramic powder



Graph 7 - Compression strength cement mortars. First ceramic powder



Graph 8 - Compression strength cement mortars. Second ceramic powder

Result of the compression test [MPa]. First ceramic powder										
	1 day	3 days	7 days	28 days	56 days	84 days				
PCEM-REF	57.1	68.2	82.2	102.9	107.0	103.4				
PCEM10	53.5	67.0	72.5	87.7	101.1	108.6				
PCEM30	37.4	55.9	60.8	77.4	82.0	83.9				
PAC-CONST30	57.4	62.7	72.0	89.3	105.1	103.7				
MCEM-REF	61.0	72.8	79.7	95.9	102.2	98.8				
MCEM10	57.0	73.3	78.7	91.4	98.2	100.7				
MCEM30	42.9	64.4	71.0	92.7	94.8	98.2				
MAC-CONST30	48.5	68.9	74.4	102.3	99.4	106.5				

Table 16 - Result of the compression test [MPa]. First ceramic powder.

Result of the compression test [MPa]. Second ceramic powder										
	1 day	3 days	7 days	28 days	56 days	84 days				
PCEM-REF	46.7	70.9	76.5	86.9	100.6	97.4				
PCEM10	40.8	78.6	86.0	88.7	107.7	102.2				
PCEM30	26.5	83.3	75.2	109.2	114.1	123.4				
PAC-CONST30	40.3	77.7	95.0	109.4	121.7	114.1				
MCEM-REF	46.8	73.3	78.2	89.1	93.3	109.9				
MCEM10	37.8	66.7	76.2	87.4	91.6	100.2				
MCEM30	21.4	45.9	52.5	66.2	69.3	62.3				
MAC-CONST30	46.8	59.3	64.5	80.7	84.8	88.9				

Table 17 - Result of the compression test [MPa]. Second ceramic powder.



Fig. 12 Typical *hourglass* shape assumed at break of the specimens subjected to the compression test

4.2.1 Mixture with volume replacement

With reference to cement pastes with the first ceramic powder it can be observed (Graph 9) that initially the PCEM-REF and PCEM10 show nearly equivalent strength values. Nevertheless, after three days starts a gap between the two curves for which the percentages of losses between PCEM10 and the PCEM-REF are close to 15%. This is due to the higher content of reactive cement in the standard mixture.

From twenty-eighth day onward, there is still an increase in the percentage of the strength in the PCEM10 higher than that of the PCEM-REF. This rise continues constant in time until, between the fifty-sixth and the eighty-fourth days, the strength of
the PCEM10 mixture exceeds that of the PCEM-REF, to the considerable value of 108.58MPa with a percentage of almost 5%. This could result from the slower but continuous pozzolanic reaction in the PCEM10.

The PCEM30 provides less interesting data. In fact, it has lower performance and a more ordinary behavior along the time, the strength stabilizing after twenty-eighth days of curing, as it happens for the PCEM-REF. The observed percentage losses are significant and constant at around 25%. From the shape of the curve, it does not seem possible a recovery of the marked gap from the other two experimental specimens.



Graph 9 - Compression strength cement pastes (volume replacement). First ceramic powder.

With reference to cement pastes with the second ceramic powder it can be observed (Graph 10) that the PCEM-REF and PCEM10 show nearly equivalent strength values along the eighty-four days, showing the PCEM10 slightly higher values than the PCEM-REF.

The PCEM30 provides initially irregular data. But in this case, the PCEM30 has a higher performance and the strength does not seems to stabilize after eighty-four days of curing, as it happens for the PCEM-REF and PCEM10 probably due to the pozzolanic effect. The observed percentage increase is significant at around 25% and 20% with respect to the PCEM-REF and PCEM10 respectively after eighty-four days.



Graph 10 - Compression strength cement pastes (volume replacement). Second ceramic powder.

Also in compression, cement mortars with the first ceramic powder (Graph 11) have more homogeneous performance than the cement pastes. To a lesser extent, the MCEM10 behavior is similar to that of the corresponding paste. The greater homogeneity among the mixtures is probably due to the presence of sand, which has a stabilizing function. At the beginning, it is perfectly comparable with the MCEM-REF, while in a second step, the path bifurcates and the percentage losses are close to 5%. As in PCEM10, the increase in terms of strength of the MCEM10 persists constantly over

time, and between the fifty-sixth and the eighty-fourth days it exceeds the reference mortar with a percentage of about 2%.

The MCEM30 after 1 day provides a lower compression strength values (on the order of 10% less than the reference mortar). Between the third and the twentyeighth days, however, it exhibits a strong increment achieving the same performance of other mixtures. From an initial analysis, it may be concluded that the ceramic powder introduction in the mortar mixture gives raise to pozzolanic reactions that are prolonged over time, which allow a reasonable comparison with the reference mixture.



Graph 11 – Compression strength cement mortars (volume replacement). First ceramic powder.

On the other hand cement mortars with the second ceramic powder (Graph 12) also have more homogeneous performance than the cement pastes. To a lesser extent, the MCEM10 behavior is similar to that of the corresponding paste and at the beginning, it is perfectly comparable with the MCEM-REF, while in a second step, the

path bifurcates and the percentage losses are close to 5%. As in PCEM10, the increase in terms of strength of the MCEM10 persists constantly over time, and between the fifty-sixth and the eighty-fourth days it exceeds the reference mortar with a percentage of about 2%.

The MCEM30 after 1 day provides a lower compression strength values (on the order of 10% less than the reference mortar). Between the third and the twentyeighth days, however, it exhibits a strong increment returning, something of other mixtures. From an initial analysis, it may be concluded that the ceramic powder introduction in the mortar mixture gives raise to pozzolanic reactions that are prolonged over time, which allow a reasonable comparison with the reference mixture.



Graph 12 - Compression strength cement mortars (volume replacement). Second ceramic powder.

4.2.2 Mixtures with constant w/c ratio

The mixtures with constant w/c ratio provide very interesting results. Analyzing the data, in fact, it is clear that this type of mixture, with longer curing period, gains a better performance compared to both, mixtures with volume cement replacement and with only Portland cement.



Graph 13 – Compression strength cement pastes (w/c=const). First ceramic powder.

In the cement paste with the first ceramic powder PAC-CONST30 (Graph 13) there is an increase in strength compared to PCEM30, due to the reasons already mentioned above (reduction of w/c ratio). After the first day of curing, from the evidence no difference is observed in terms of strength with the reference cement paste, although, with increasing aging time, it appears a gap in the performance losses compared to PCEM-REF. Such losses (around 10%) are half of those compared to PCEM30. The divergence tends to fade away with increasing curing: it can be noted

that on the fifty-sixth day after casting the difference with the PCEM-REF is almost nothing.



Graph 14 – Compression strength cement pastes (w/c=const). Second ceramic powder.

In the cement paste with the second ceramic powder, up to the third day of curing no difference is observed in terms of strength with the reference cement paste, although, with increasing aging time, between the seventh and the fifty-fourth day it appears a constant gain of about 20% in the performance compared to PCEM-REF. The divergence tends to decrease slightly for eighty-fourth days.



Graph 15 – Compression strength cement mortars (*w/c=const*). *First ceramic powder*.

Similar considerations can be made for the cement mortar with the first ceramic powder (Graph 15). The MAC-CONST30 is immediately competitive with the mortar with only Portland. Since the third day after casting the strengths comparable with the reference mortar were recorded. The pozzolanic reaction would seem to have more rapid effects and pronounced than the cement paste related, but also less prolonged in time. At 56 days of curing, the results presented by the MAC-CONST30 are the same to those of the MCEM-REF.



Graph 16 – Compression strength cement mortars (w/c=const). Second ceramic powder.

On the other hand the MAC-CONST30 with the second ceramic powder is immediately competitive with the MCEM-REF and also from the third day the strength of the MAC-CONST30 is clearly higher with a constant gap between the twenty-eighth and the fifty-fourth days and this difference increases for eighty-eight days.

4.3 Results of the flexural test

All the flexural strength data recorded appear in table 18 and 19 for both types of ceramic powder mixtures.

Results of the flexural test [MPa]									
	1 day	3 day	7 day	28 day	56 day	84 day			
PCEM-REF	9.3	6.5	6.0	6.8	-	5.1			
PCEM10	7.0	6.8	6.3	6.5	-	3.5			
PCEM30	7.0	6.1	5.2	5.4	-	2.5			
PAC-CONST30	6.3	6.2	7.9	5.6	6.3	7.4			
MCEM-REF	9.1	10.4	12.4	12.6	11.9	10.5			
MCEM10	8.0	9.1	11.7	10.7	10.8	9.8			
MCEM30	7.1	7.9	9.6	10.6	9.9	9.4			
MAC-CONST30	8.0	11.8	12.8	10.6	13.7	15.0			

Table 18 - Results of the flexural test for the first ceramic powder [MPa]

Results of the flexural test [MPa]									
	1 day	3 day	7 day	28 day	56 day	84 day			
PCEM-REF	7.0	10.2	7.7	6.2	9.8	8.1			
PCEM10	8.0	11.6	8.6	6.3	6.9	5.6			
PCEM30	6.0	10.2	8.2	7.6	10.6	11.3			
PAC-CONST30	6.9	11.1	7.0	7.1	7.6	6.6			
MCEM-REF	8.3	8.3	13.4	13.0	12.1	12.9			
MCEM10	6.8	9.1	13.6	12.7	12.7	11.4			
MCEM30	4.6	7.9	10.4	10.7	10.4	10.8			
MAC-CONST30	8.4	9.0	13.7	12.5	13.4	14.5			

Table 19 - Results of the flexural test for the second ceramic powder [MPa]

4.3.1 Mixture with volume replacement

The flexural strength development for the pastes made with the first ceramic powder is shown in Graph 17. For all percentages of substitution of ceramic powder it seems to be associable with the own behavior of the cement paste, more deformable (i.e. more capable of redistributing stresses on the cross-section level) at early maturation and more brittle over the long term.

The curve of the specimens made with replacement of 10% of cement is, until the 28 days of curing perfectly superimposable with that of standard mixtures; the differences are, in fact, lower than 5%. On the contrary, the pastes with 30% cement replacement ratio show lower performances and losses in terms of flexure strength exceed 20%.

In the long term the PCEM10 undergoes a decrease in terms of flexural strength with losses that exceeds 30% while the PCEM30 losses are of about 50%.



Graph 17 – Flexural strength of cement pastes (volume replacement). First ceramic powder.

However for the second ceramic powder the flexural strength values shown in the Graph 18 do not follow a clear pattern.

In the case of the 30% of ceramic replacement, the specimens seem to become more ductile over the time, while for the reference and 10% of ceramic replacement mixtures, the curves tend to fluctuate without displaying a particular trend.

Once again the curve of the specimens made with replacement of 10% of cement is, until the 28 days of curing perfectly superimposable with that of standard mixtures. But in contrast, for the second ceramic powder the pastes with 30% cement replacement show higher performances reaching values up to 40% higher than the reference ones.



Graph 18 - Flexural strength of cement pastes (volume replacement). Second ceramic powder.

With reference to cement mortars prepared with the first ceramic powder (Graph 19), it should be noted the substantial achievement of a steady value of the flexural strength for all the mixtures. Furthermore, compared to the case of the pastes, it is noted an attenuation of the differences between the three mixtures and this is attributed to the presence of sand, which remains unchanged in quantity while varying the percentage of ceramic, conferring greater stability to the mortars. Even in this case, lower strength values were obtained for higher cement replacement values.

Differences with respect to the reference mixture are anyway smaller than in the case of pastes.

Also the decreasing trend for larger curing ages appears to be lower than for pastes, once again most likely due to the stabilizing effect of sand.



Graph 19 - Flexural strength of cement mortars (volume replacement). First ceramic powder.

Also with reference to cement mortars prepared with the second ceramic powder (Graph 20), the substantial achievement of a steady value of the flexural strength for all the mixtures should be noted and, compared to the case of the pastes, it is noted an attenuation of the differences between the three mixtures and this is attributed to the presence of sand, which remains unchanged in quantity while varying the percentage of ceramic, conferring greater stability to the mortars like in the case of the first ceramic powder.



Graph 20 – Flexural strength of cement mortars (volume replacement). Second ceramic powder.

4.3.2 Mixtures with constant w/c ratio

For both cement pastes and mortars (graphs 21, 22, 23 and 24) the cement replacement keeping the w/c ratio constant, provides strength values similar to the reference ones, improving the results with respect to the mixtures without keeping the w/c ratio constant.



Graph 21 – Flexural strength of cement pastes (w/c = const). First ceramic powder.



Graph 22 – Flexural strength of cement pastes (w/c = const). Second ceramic powder.



Graph 23 – Flexural strength of cement mortars (w/c = const). First ceramic powder.



Graph 24 – Flexural strength of cement mortars (w/c = const). Second ceramic powder.

4.4 Results of shrinkage test

The graphical representation of the results will be presented in the ensuing section. Each graph shall represent each mixture; and for each graph 3 curves will be presented. Each curve will represent the evolution of the shrinkage strain. One of these curves will represent the autogenous shrinkage and will denoted as such, and the remaining will represent the total shrinkage in a 50% relative humidity environment.

The control variables for this test are:



Graph 25 - Shrinkage Test PCEM-REF (Cement Paste with no ceramic substitution)



Graph 26 – Shrinkage Test MCEM-REF (Mortar with no ceramic substitution)

4.4.1 Ceramic Powder #1

4.4.1.a Cement Paste



Graph 27 – Shrinkage Test PCEM10 (Cement Paste with 10% ceramic substitution)



Graph 28 – Shrinkage Test PCEM30 (Cement Paste with 30% ceramic substitution)

The reduction of the final shrinkage of PCEM10 with respect to the reference is of about 5%. While PCEM30 presents no improvement, furthermore the final shrinkage strain is 4% greater, on average, than the reference specimen. Conversely, when only considering autogenous shrinkage PCEM30 (10% strain reduction) performs better than PCEM10 which does not improve the physical behavior (5% strain increase). The strain rate of the initial curve is rather similar for PCEM-REF, PCEM10 and PCEM30; all achieve 50% of the final strain around the fifth day. The rate of increase for the second part of the curve is slightly increased on the specimens with ceramic substitution. These specimens achieve 80% of the total shrinkage strain two days earlier, on average, than the reference mixture.



Graph 29 – Shrinkage Test PAC-CONST30 (Cement Paste with 30% ceramic substitution and water cement ratio constant)

PAC-CONST30 presents an amply improved shrinkage behavior. The final shrinkage is reduced 30%, on average, with respect to the average specimen. In the case when only autogenous shrinkage is permitted, the improvement is sustained with a 20% strain reduction. On the other hand, the strain rate is increased; the 50% of the total strain is achieved around the third day and the 80% is achieved around the sixth day.



Graph 30 – Shrinkage Test MCEM10 (Mortar with 10% ceramic substitution)



Graph 31 – Shrinkage Test MCEM30 (Mortar with 30% ceramic substitution)

Interestingly the outcome with the mortar tests is more favorable than the cement pastes. MCEM10 presents a 10% decrease of the total shrinkage strain, while MCEM30 yields a 20% strain decrease. The enhanced performance is maintained when only autogenous behavior is considered as well. MCEM10 presents a 25% improvement and MCEM30 presents a 30% improvement. In regards to the strain rate, the first days are practically the same for MCEM-REF, MCEM10 and MCEM30; for latter days this rate is slightly increased in direct proportion to the amount of ceramic powder.



Graph 32 – Shrinkage Test MAC-CONST30 (Mortar with 30% ceramic substitution and water-cement ratio constant)

The positive effect of the cement powder #1 on the shrinkage strain can still be appreciated on MAC-CONST30. There is a total shrinkage strain reduction of around 30% and a reduction of the autogenous strain by the same proportion. The strain rate on the first days is similar for MAC-CONST30 and MCEM-REF. The 50% of the total shrinkage strain is achieved around the third day for both cases, but this rate is

increased for MAC-CONST30 as the test continues. MAC-CONST30 reaches the 80% of the total strain around the fifth day, while MCEM-REF reaches it around the tenth day.

4.4.2 Ceramic Powder #2

4.4.2.a Cement Paste



Graph 33 – Shrinkage Test PCEM10 (Cement Paste with 10% ceramic substitution)



Graph 34 – Shrinkage Test PCEM30 (Cement Paste with 30% ceramic substitution)

From the results obtained for the cement paste it can be noted that between PCEM-REF and PCEM10, there is no improvement in the obtained final shrinkage strain. The total shrinkage is 10% greater on PCEM10, whilst the autogenous shrinkage is the same for both. Conversely PCEM30 presents a 50% reduction on the final shrinkage strain magnitude of the total and autogenous shrinkage. The rate of evolution of shrinkage on all the cement paste mixes is rather similar. All the samples reach 50% of the total inelastic strain around the fifth day, and reach 80% around the sixteenth day. The sealed specimens on the other hand present a reduced rate of shrinkage proportional to the amount of cement powder substitution.



Graph 35 – Shrinkage Test PAC-CONST30 (Cement Paste with 30% ceramic substitution and water cement ratio constant)

As noted before a 30% substitution of cement powder with ceramic powder has a notorious effect in reducing the shrinkage strain. PAC-CONST30 expectedly presents the same tendency, but the final strain is $1^{0}/_{00}$ greater in average with respect to PCEM30. In other words, shrinkage tendency is improved, but not as effectively as for the PCEM30 proportions. The rate of shrinkage is similar to the three previous results; a 50% of the shrinkage strain is achieved around 5 days. However a slight difference is observed after this point, PCEM-CONST30 presents a small increase in rate with respect to the other. To clarify, it can be stated that the 80% of the shrinkage strain for PAC-CONST30 is attained around day 11 for the specimen exposed to the environment, and at around day 22 for the sealed specimen.

4.4.2.b Mortar



Graph 36 – Shrinkage Test MCEM10 (Mortar with 10% ceramic substitution)



Graph 37 – Shrinkage Test MCEM30 (Mortar with 30% ceramic substitution)

Interestingly, mortar tests with the ceramic powder #2 are presenting positive results for shrinkage behavior. The difference in the final shrinkage strain between MCEM-REF and MCEM10 can be approximated to a 10% decrease of the total shrinkage and a 20% decrease if only autogenous shrinkage is considered. Moreover MCEM30 presents a 30% improvement, in average, of the final total shrinkage with respect to MCEM-REF. In relation to the rate of total shrinkage strain, the 50% is achieved around the third day, except for MCEM30 on which occurs approximately 2 days later. After this point the rate of shrinkage for MCEM10 is slightly reduced with respect to the other mortar mixes which tend to the same rate between them.



Graph 38 – Shrinkage Test MAC-CONST30 (Mortar with 30% ceramic substitution and water-cement ratio constant)

Similarly as for what was has been observed so far, the shrinkage behavior of MAC-CONST30 is favorable for engineering purposes. Compared to MCEM-REF the improvement is of about 35% for total shrinkage and isolated autogenous shrinkage.

The rate of shrinkage for this mixture is reduced to a value less than any mortar studied before. The 50% of the total shrinkage is achieved around six days and the 80% is reached around the thirteenth day.

4.4.3 Synthesis of Shrinkage Tests

The following graphs present a summary of the results obtained on the shrinkage test.



Graph 39 – Superposition of Shrinkage Tests Performed to Different Cement Pastes Elaborated with the Ceramic Powder #1



Graph 40 – Superposition of Shrinkage Tests Performed to Different Mortars Elaborated with the Ceramic Powder #1



Graph 41 – Superposition of Shrinkage Tests Performed to Different Cement Pastes Elaborated with the Ceramic Powder #2



Graph 42 – Superposition of Shrinkage Tests Performed to Different Mortars Elaborated with the Ceramic Powder #2

OBSERVATIONS AND CONCLUSIONS

In this work, from the results obtained from mechanical tests it can be stated that, in general the ceramic powder introduction does not affect the performance of the mixtures to the point of invalidating the generic project requirements. In some cases, however, the added ceramic induces pozzolanic reactions able to make the new mix even better performing than the reference ones, especially in the long term. Mixtures containing ceramic powder are in fact competitive with standard mixtures, especially in the compression test, while less brilliant is the effect for the flexural tests.

In general, from the previous experiments it can be concluded that:

- The mixtures designed keeping the w/c ratio constant provide a higher performance and more homogeneous strength values varying the ceramic content;
- The percentage losses in terms of strength with respect to the reference mixtures are accentuated for cement pastes, while they remain limited in the case of mortars and this means that for the case of concrete can be obtained even better results;
- Regarding the first ceramic powder in PCEM10, MCEM10, MCEM30, PAC-CONST30 and MAC-CONST30 many indications were found of a possible pozzolanic activity. In the case of the second ceramic powder in PCEM30, MCEM10, MCEM30, PAC-CONST30 and MAC-CONST30.

Making a comparison between the two ceramic powders it can be stated that:

- In compression tests, in the case of cement pastes the second ceramic powder gives higher resistance values for both keeping constant the w/c ratio and without keeping it.
- In compression tests, in the case of cement mortars the first ceramic powder gives a better performance for both instances, keeping constant the w/c ratio and without keeping it.
- In flexural tests, even though the values fluctuate and are unpredictable, it can be stated that in general the second ceramic gives higher resistance values for all different mixtures.

The results must be interpreted in light of the fact that the cement used - CEM I 52.5R - is a high performance cement. It seems plausible then that the products resulting from the pozzolanic process, as resistant, are not able to supply adequate strength recovery for a high cement subtraction. For this reason, the blends designed by cement volume replacement are more affected, compared to those made without ceramic powder addition, as percentages of strength deficiencies. The volume replacement, in fact, entails a reduction in the amount of cement that for the mixes with 30%, appears to be significant. It is therefore considered that, even if present, the pozzolanic activity in this kind of mixtures is not able to significantly gain back the resistance. However, a more careful analysis cannot ignore the fact that some of the replacement mixtures can still achieve the same values of the mixtures containing only Portland, which should be interpreted as an index of the performance level that the pozzolan conferred through the ceramic material. It is therefore logic to assume that the ceramic powder introduction produces greater benefits when used as a replacement of less performing cement as base binder, situation definitely more frequent.

The resistance differences obtained by varying the ceramic content for the cement pastes with respect to the cement mortars can be associated to the fact that, in the first ones, the only constituent providing resistance is the cement which is replaced by the ceramic powder with possesses much lower initial resistance, even though, pozzolanic reactions help to redifine the resistance in the long term.

In contrast, in all mortar mixes it is present a constant quantity of sand. This one, acting as inert, plays a stabilizing action varying the ceramic content as it contributes in an equivalent manner for all mixes to define the resistance of the final product. For this reason, the ceramic content variation results in a lower impact on the strength of the mortars and the various mixtures provide more homogeneous data. In the wake of this, one can therefore assume that the introduction of ceramic powder in the production of concretes will involve even minor differences, since the quantity of aggregates increases.

However, the dosage of the ceramic powder must be taken into account. Previous researches have in fact detected a maximum percentage in the ceramic powder added to cement of 35% beyond which the mechanical properties begin to worsen, probably due to the absence of sufficient calcium hydroxide to react with the pozzolanic substances or for the slowness of the pozzolanic-reaction itself.

In this case, also the mixtures manufactured with the same criterion (removal of cement and ceramic insertion) reach and far exceed (approximately 10MPa) the preset limits for the mixture of Portland only at 28 days. Therefore, the value of these thresholds should be computed as a function of the pozzolanic activity indices of the blends (measurable by means of the Chapelle method. for example, or with the Frattini test) and of reactivity indices.

Note, however, that only the PCEM30 with the first ceramic and MCEM30 with the second ceramic show percentage losses in terms of resistance constantly above 20%, which could invalidate the use for structural elements of a certain importance. Nevertheless, even these mixtures (like the others) could still be used for lower performance structural elements such as curbs, roof tiles, and all other elements in the world of prefabricated concrete of small and average size for which a strongly performance binder is not necessary. These elements that represent a large share within the construction industry for which the economic and environmental benefits would still be relevant.

With reference to the other mixtures, they provide a comparable performance with those of the mixtures of Portland only. It is therefore appropriate to consider them to be further investigated, as they may be also valid for relevant structural commitments.

Referring to the shrinkage behavior of mixes with the Ceramic Powder #1, a bare substitution of cement with the ceramic powder yields mixed results for cement paste and mortar. It can be stated that the cement paste's behavior does not improve with this approach; conversely mortar is positively affected by the substitution. Instead keeping the water-cement ratio constant causes the shrinkage behavior of both cement paste and mortar to be greatly improved.

Referring to the shrinkage behavior of mixes with the Ceramic Powder #2 it becomes apparent that the use of this ceramic has a positive impact on the shrinkage behavior. The cement paste with a bare substitution of 10% of cement yields approximately the same behavior as the reference mix, however a 30% substitution presents remarkable results. A pattern between the amount of cement substitution and the shrinkage strain is apparent. The mortar mixtures demonstrate a similar pattern, with the exception that mortar is benefited even with only a 10% substitution. Similarly to the Ceramic Powder #1, maintaining the water cement ratio produces excellent results for shrinkage reduction.

Finally, the strain rate for each test has been commented on the previous shrinkage section of this paper. It can be concluded, in a general sense, that the strain rate is not affected in any significant manner for engineering purposes. However it can be noted that the Ceramic Powder #1 causes the strain rate to accelerate, referred to the control variable, for any kind of mixture studied. Inversely, the Ceramic Powder #2 decreases the strain rate with reference to the control variable.

Therefore, the results in this study obtained, seem congruous with the data from earlier experiments, and future developments could be directed to assess how this increase of curing time affects on costs and timing.

In conclusion, it is at least clear that the use of ceramic recycle material in the production of cement pastes, mortars and concretes is a valid discussion and interesting topic, and comprising several applications in which countless strategies are yet to emerge. Therefore future researches related to the study of concrete properties will be performed since losses in mortars remain limited due to the stabilizing effect of the sand, and in the case of concrete by using both fine and coarse aggregates (the latter ignored in the experiments) the ratio between the cement and the aggregates is smaller being able to increase the stabilizing effect observed in mortars. In addition durability in concrete specimens will be an interesting characteristic to analyse in future researches.

6

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Furthermore, it was a great assistance to read:

- L. Bertolini. "Materiali da costruzione". capp. 7-10;
- Eurocode 196-1. sgg.