Thermal Behavior of Different Concrete Mixtures with Pozzolanic Additions

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ABSTRACT The hydration process of cement is an exothermic chemical reaction; the evolution of heat generated during hardening of concrete causes, especially in structures and massive elements, differential contractions between the nucleus and the surface that might generate large thermal shrinkage cracks. The current study wants to identify the factors which allow to obtain the biggest reduction of the heat of hydration using the products with pozzolanic effect present on the market, such as GGBS, silica fume ad fly ash. The goal is to prepare a recipe with a proper proportion of pozzolanic materials able to reduce the heat of hydration of concrete through a reduction of the amount of cement but without affecting the long term compressive strengths. After identifying the best pozzolanic compound, this study wants to propose an analytical method to assign an efficiency factor to the powder mixture, in order to work out the amount of equivalent cement to replace. Thanks to adiabatic calorimetry, it has been possible to experimentally evaluate the heat generated by a series of concrete samples designed with different amounts of pozzolanic materials. Comparing the best performance in terms of compressive strength and reduction of the heat of hydration, the most promising experimental product was identified. This product has been subsequently validated by field trial tests. Some field application of the final product which was performed in several important construction sites, will be showed and documented.

1 INTRODUCTION

Silica fume is a byproduct from the production of silicon and ferrosilicon alloys in electric arc furnaces. It consists of fine vitreous particles with a surface area on the order of 20.000 m²/kg and particles approximately one hundredth the size of the average cement particle (ACI, 2006). Because of its extreme fineness and high amorphous silica (SiO_2) content, silica fume is a very effective pozzolanic material (ACI, 1987; ASTM, 2012). Standard specifications for silica fume used in cementitious mixtures are ASTM C1240 (ASTM, 2012), EN 13263 (CEN,2005) Prior to the mid-1970s, nearly all silica fume was discharged into the atmosphere. After environmental concerns necessitated the collection and landfilling of silica fume, it became economically viable to use silica fume in various applications, as high-performance concrete production. Silica fume is added to Portland cement concrete to improve its properties, in particular its compressive strength, bond strength, and abrasion resistance. These benefits derive from both the mechanical improvements resulting from addition of a very fine powder to the cement paste (filling properties) as well as from the pozzolanic reaction between the silica fume and free calcium hydroxide in the paste. Addition of silica fume also reduces the permeability of concrete to chloride ions, which protects the reinforcing steel of concrete from corrosion, especially in chloride-rich environments. Incorporating silica fume into concrete mixtures also reduces bleeding significantly because the free water is consumed in

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wetting of the large surface area of the silica fume particles, which also tends to blocks pores in the fresh concrete preventing water from coming to the surface. The mentioned improvement in concrete, both in its fresh and hard state, are usually reached with dosages of SF in the range of 5-10% of the weight of cement in the mixture.

Ground granulated blast furnace slag (GGBS or GGBFS) is obtained by quenching molten iron slag (a by-product of iron and steel making) from a blast furnace, to produce a glassy, granular product that is then dried and ground into a fine powder. Since GGBS is a by-product of steel manufacturing process, its use in concrete is recognized, for example by LEED, as improving the sustainability of the projects, especially if used for superstructure and in addition to the cases where the concrete is in contact with chlorides and sulfates. Actually, GGBS is routinely used to limit the temperature rise in large concrete pours. The more gradual hydration of GGBS cement generates both lower peak and less total overall heat than Portland cement. This reduces thermal gradients in the concrete, which prevents the occurrence of microcracking which can weaken the concrete and reduce its durability. Concrete containing GGBS tends to have higher ultimate strength than concrete made with Portland cement only, mainly because of the higher proportion of the strength-enhancing calcium silicate hydrates (CSH) than in concrete made with Portland cement only, and a reduced content of free lime, which does not contribute to concrete strength. In fact, concrete made with GGBS continues to gain strength over time, and has been shown to double its 28-day strength over periods of 10 to 12 years. Although replacement of the Portland cement with GGBS may be made in a wide range of percentages by weight (from 30% to up to 85% of the original cement dosage), 40 to 50% is used in most instances. In this study a comparative analysis among concrete mixtures prepared with different percentages of cement replaced with ternary combinations of calcareous filler, silica fume and fine grounded blast furnace slag was carried out. The mentioned combinations of secondary cementitious materials have been named Compound PZ A, compound PZ B, and compound PZ C respectively, and the correspondent efficiency factors were evaluated. Preliminary results are reported in terms of variation in concrete compressive strength and temperature evolution measured in adiabatic conditions.

2 MATERIALS AND SETTINGS

A series of three reference concrete mixtures were prepared adopting various dosage of Cement II/A-LL 42,5R supplied by an Italian producer while the amount of mixing water was kept constant as shown in the following Table 1. Admixture type superplasticizer was incorporated into mixtures in the range of 0,9-1,0% of the cement weight to obtain good rheology.

Table 1. Cement and water dosages for the reference concrete mixtures: resulting compressive strength values.

Ref. mix-ture #	**Cement**	**Water**			**air (%)**	**Slump (mm) UNI EN 12350-3 *(after 7')***	**Compressive Strength (MPa) (at 20°C and 95%RH)**							
	Kg/m³	*L/m³*	*w/binder*	*w/c*			***7dd***	*Weight kg/m³*	***28dd***	*Weight kg/m³*	***60dd***	*Weight kg/m³*	***90dd***	*Weight kg/m³*
1	248	**195**	0,77	0,78	3,6	235	21,1	2286	24,1	2248	27,8	2265	28,3	2267
2	298	**195**	0,65	0,65	2,5	200	28,4	2295	34,7	2289	39,1	2295	40,0	2319
3	348	**195**	0,56	0,56	2,7	210	33,0	2303	42,0	2287	46,1	2296	48,3	2299

Three different values of the water to cement ratio resulted (0,78; 0,65 and 0,56 respectively), and the concrete compressive strength at the age of 7, 28, 60 and 90 days were recorded for all the mixtures. Figure 1 shows the variation in compressive strength at the age of 28 days as result of increased water to cement ratios.

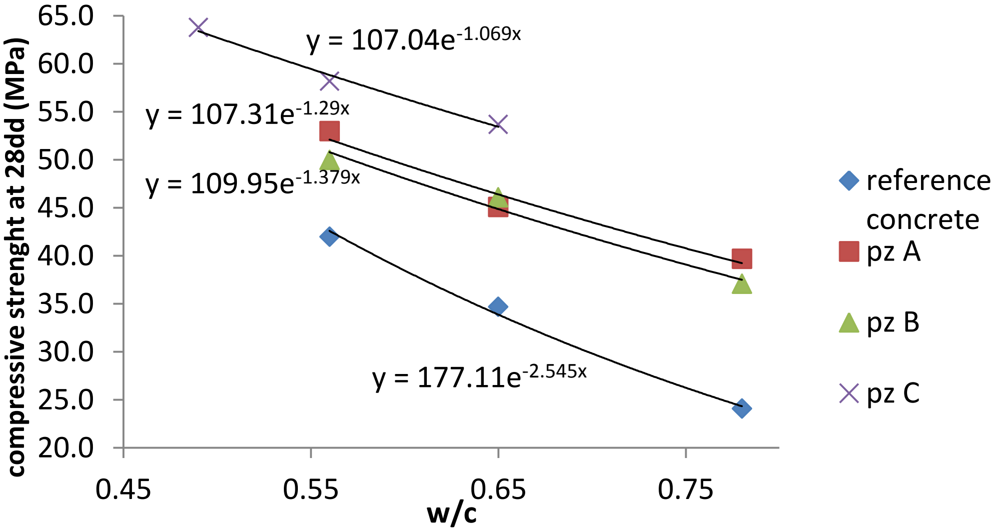

Figure 1. Concrete compressive strength (measured at 28 days from cast) as function of the water to cement ratio: experimental regressions.

Three ternary combinations of calcareous filler, silica fume and fine grounded blast furnace slag were prepared varying the silica fume to slag ratio while the amount of the calcareous filler was kept constant: unfortunately, precise proportions among single ingredients could not be provided in this paper because of commercial policy. Mentioned combinations, hereafter referred to as “ternary compounds” or simply “compounds”, have been named compound PZ A, PZ B, and PZ C respectively, and the correspondent efficiency factors have been evaluated. Determination of the efficiency factors was made possible by the preliminary execution of the following steps:
Step 1: 100 kg of compound PZ A was added to reference mixtures 1, 2 and 3 listed in Table 1, and new concrete mixtures named 1001, 1002, and 1003 respectively were obtained: their composition is shown in table 2. Amount of the aggregates (sand and gravel) is adjusted to compensate for the addition of the fillers. Admixture dosage is calibrated to maintain the good rheology of the mixtures.

Table 2. Cement and water dosages for concrete mixtures including compounds: resulting compressive strength values.

Mixture #	**Addition**		**Cement Kg/m3**	**Water**			*density Kg/m³*	**Air (%)**	**Slump (mm) UNI EN 12350-3 (mm after 7')**	**Compressive Strength (MPa) (at 20°C and 95%RU)**							
	Type	*Dosage Kg/m³*		*l/m³*	*w/ binder*	*w/c*				***7dd***	*density kg/m³*	***28dd***	*density kg/m³*	***60dd***	*density kg/m³*	***90dd***	*density kg/m³*
1001	PZ A	100	251	195	0,56	0,78	2310	3,2	180	**27,3**	2301	**39,7**	2312	**45,2**	2318	**47,1**	2312
1002	PZ A	100	302	195	0,49	0,65	2322	2,8	210	**34,0**	2315	**45,1**	2316	**51,1**	2318	**56,0**	2319
1003	PZ A	100	351	195	0,43	0,56	2326	3,0	210	**39,3**	2320	**53,0**	2304	**56,2**	2312	**61,2**	2335
2001	PZ B	100	250	195	0,56	0,78	2306	3,4	175	**25,4**	2281	**37,1**	2286	**40,0**	2273	**41,1**	2280
2002	PZ B	100	300	195	0,49	0,65	2313	3,6	170	**35,4**	2287	**46,1**	2308	**49,9**	2308	**54,4**	2317
2003	PZ B	100	350	195	0,43	0,56	2322	2,9	210	**39,3**	2298	**50,0**	2305	**57,8**	2305	**58,5**	2303
3001	PZ C	150	299	195	0,43	0,65	2300	3,0	210	**37,5**	2300	**46,7**	2295	**53,7**	2322	**58,8**	2302
3002	PZ C	150	350	195	0,39	0,56	2314	3,2	210	**39,2**	2268	**49,3**	2287	**58,2**	2286	**61,3**	2279
3003	PZ C	150	400	195	0,35	0,49	2316	3,3	210	**38,9**	2307	**54,9**	2291	**63,8**	2296	**67,1**	2293

Step 2: For the concrete mixtures obtained as in Step 1, values of the compressive strength were experimentally determined at the age of 7, 28, 60 and 90 days after cast, and data recorded as in Table 2.

Step 3: Step 1 and 2 were repeated for compounds PZ A and PZ B respectively so obtain concrete mixtures 2001, 2002, 2003 as well as 3001, 3002, 3003. In Table 2 corresponding data of compressive strength at different ages are reported.

Step 4: Data from Table 2 are plotted in terms of compressive strength values vs. the water to cement ratios, so determining an experimental low (exponential type $Rc = a_* e^{b*(w/c)}$) for each of the three compounds. Data in Figure 1 refers to compressive strength values measured at the age of 28days from the cast. Similar plots are obtained when strength values at different ages are considered.

Step 5: Numerical coefficient *a* and *b* of the regressions laws plotted as in Step 4 are recorded. Table 3 resumes the coefficients of all the regression, referring to any different series of concrete mixtures at any different age of tests. Concerning compressive strength values at the age of 28 days, coefficient *a* and *b* are listed in Table 3 as they are readable from Fig. 1.

Table 3. Coefficients a and b of the experimental regressions (exponential lows type $Rc = a_* e^{b*(w/c)}$): data shown in Fig. 1 are marked in bold style

Mixture	**7 days**			**28days**			**60 days**			**90 days**		
	a	*b*	*R²*	*a*	*b*	*R²*	*a*	*b*	*R²*	*a*	*b*	*R²*
Reference	105.4	-2.051	0.99	**177.11**	**-2.545**	**0.99**	205.76	-2.462	0.71	188.32	-2.43	1
Including PZ A	99.64	-1.658	0.99	**107.31**	**-1.290**	**0.97**	97.44	-0.987	0.99	120.72	-1.200	0.99
Including PZ B	125.68	-2.024	0.97	**109.95**	**-1.379**	**0.98**	147.90	-1.675	0.99	151.03	-1.644	0.95
Including PZ C	44.17	-0.241	0.67	**107.04**	**-1.069**	**0.99**	98.51	-0.808	0.92	102.85	-0.756	0.95

3 DETERMINATION OF THE EFFICIENCY FACTORS

Once the experimental laws among concrete compressive strength and water to cement ratios are available (namely the characteristic laws), a target value for the concrete compressive strength Rc may be selected and the correspondent efficiency factor k determined for any given compounds as it follows.

First, the w/c ratio needed to obtain the desired compressive strength is determined inverting the characteristic law: for instance, required w/c ratio to obtain Rc = 30 MPa at the age of 28 days from reference mixture (incorporating only plain cement) is w/c = 0.7. Considering mixtures incorporating compound PZ A, PZ B and PZ C, the following w/c values are found: 0.99, 0.94 and 1.19. Since characteristic laws of all mixtures were obtained varying the w/c ratios while keeping water dosage constant (195 lt/m^3), different cement dosages resulted among reference mixtures and those incorporating compounds. This differences in cement dosage compared to the amount on compound adopted (fixed to 100 kg for compounds PZ A and PZ B and to150kg for compound PZ C) allows to evaluate efficiency factors. Going into details, 280 kg/m^3 of plain cement are needed to obtain Rc = 30 MPa at the age of 28 days from reference mixture (w/c= 0.7, water = 195 kg/m^3, consequently c= 195/0.7=280 Kg/m^3); dosage of cement reduces to 197 kg/m^3 when concrete mixture incorporating 100 kg of compound PZ A is considered: saving of 82 kg/m^3 of cement results (280-197=82), and efficiency factor corresponding to compound PZ A for compressive strength of 30MPa at the age of 28days is evaluated as $k_{PZ\ A,30,28}$ = 82/100 = 0.82.

Computing k values for all the considered compounds, with respect to various target values for the concrete compressive strength (Rc = 20, 30 and 40 MPa respectively) and for various ages of the concrete (28, 60 and 90 days respectively), data listed in Table 4 were obtained.

Table 4. Efficiency factors corresponding to various compressive strength target and ages of the concrete

target compressive strength	age	K		
		Mixture including compound PZ A	Mixture including compound PZ B	Mixture including compound PZ C
20 MPa	28 days	0,78	0,7	0,69
	60 days	0,89	0,47	0,74
	90 days	0,81	0,52	0,8
30 MPa	28 days	0,82	0,72	0,77
	60 days	0,96	0,55	0,85
	90 days	0,89	0,58	0,91
40 MPa	28 days	0,79	0,68	0,81
	60 days	0,94	0,61	0,9
	90 days	0,92	0,62	0,98
average		**0,87**	**0,61**	**0,83**

4 RESULTS AND DISCUSSION

To validate the estimation of the efficiency factors, three new concrete mixtures (named RefMix, MixPZ A, MixPZ B and MixPZ C, respectively) have been prepared and tested to compare compressive strength evolution and heat released during cement hydration. Details concerning concrete mixtures compositions in terms of cement and compounds dosages are provided in Table 5. Cement type CEM II A-LL 42,5 was adopted and a small amount of admixture type superplasticiser (0.9% of the cement weight) was incorporated into mixtures to obtain a satisfactory rheology. Data of concrete compressive strength experimentally measured at the ages of 7 and 28 days respectively have been also reported in Table 5.

Table 5. Validating tests: cement and water dosages of the concrete mixtures and resulting compressive strength values.

Mixture #	**Addition**		**Cement**	**Water**			**den-sity** Kg/m^3	**Air** (%)	**Slump UNI EN 12350-3 (mm after 7')**	**Compressive Strength (MPa) (at 20°C and 95%RU)**	
	Type	Dosage Kg/m³	Kg/m³	lt/m³	w/binder	w/c				**7dd**	**28dd**
RefMix	-	-	350	194	0,55	0,55	2340	2,3	220	37,3	44,6
MixPZ A	PZ A	100	260	194	0,54	0,75	2325	2,2	220	26,8	36,1
MixPZ B	PZ B	100	290	194	0,50	0,67	2325	2,2	220	31,4	41,3
MixPZ C	PZ C	100	270	194	0,52	0,72	2274	3,8	220	26,2	37,1

Figure 2 shows the graph of the temperature measured by an adiabatic calorimeter during the setting of the concrete mixtures listed in Table 5. As expected, mixtures incorporating any of the compounds in partial substitution of the original cement dosage of 350 Kg/m^3 in RefMix, showed to reach lower temperature during setting compared to RefMix (incorporating only cement).

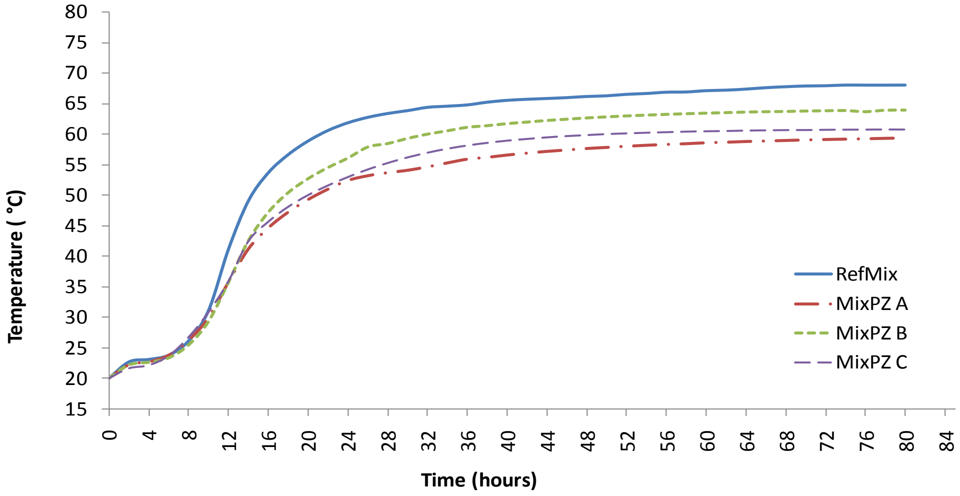

Figure 2. Heat release in adiabatic calorimeter: temperature evolution during concrete setting

Compared to compounds PZ B and PZ C respectively, curve corresponding to MixPZ A resulted to be the lowest in the graph so indicating compound PZ A as the most effective in reducing heat release during concrete setting. However, experimental values of the 28 days concrete compressive strength corresponding to MixPZ A (36.1 MPa) resulted to be the lowest among all mixtures (last column in Tab 5), and difference of about 8.5MPa with reference value (44.6MPa for RefMix) may not be ignored. This would advice for a better calibration of the cement substitution when operating with compounds PZ A, although potential of this specific compound is believed to remain the most promising in comparison with other compounds PZ B and PZ C respectively.

5 CASE STUDY

The present case of study refers to the just built (2012) mat foundation of a new tower currently under construction in the CityLife district of Milan. The tower has been designed by Arata Isozaki and Andrea Maffei and by 2015 it will reach the final height of about 207 meters, representing the tallest skyscraper in Italy. A grid of 62 underpinning piles measuring over 30 m in length has already been constructed out of reinforced concrete to sustain the building foundation. The mat foundation bed, covers a rectangular area of about 63 m x 27 m and it is formed of a single, massive reinforced concrete block measuring about 2.5 m in thickness (somewhere up to 3.5 m) and occupying a total volume of about 4200 m^3. To speed up the construction process and due to the reinforcing bars congestion, building foundation was built in SCC and accomplished in 30 hours of uninterrupted concrete pour. Concrete compressive strength was fixed to C32/40 MPa and specific requirements had to be satisfied in terms of concrete rheology and thermal properties as well. In fact, due to the casting dimensions and to the usual cement content characterizing SCC mixtures, the project had obviously to be regarded as a mass concrete case, thus taking precautions to prevent thermal cracking of the structure. In this case study, designers prescribed the concrete maximum temperature difference not to exceed 20 °C.

To realize the complex project and to speed up the construction process, both the concrete producer and the additions/chemicals supplier (Mapei) decided to use the pozzolanic addition PZ A (commercially available as Mapeplast PZ300) selected from the experimental work in the lab to prepare a tailor made low heat SCC mixture to be poured as a unique SCC massive cast to be accomplished in about 30 hours of uninterrupted work. This specific choice was taken in collaboration with the general contractor and the superintendent of works as well.

The following Table 6 summarizes the optimum SCC mixture composition selected for the project.

At the constructions field, fresh concrete properties were tested both at the mixing plant (by the concrete producer) and at the building side (by the Mapei Mobile laboratory). Test procedure included visual controls before any new concrete discharge, measurement of the slump flow and determination of T50, V-funnel and the J-ring values (every 100 m^3 of concrete). Monitoring of the concrete compressive strength was, instead, carried out at different ages on concrete samples taken during the concrete placement. A total number of 58 couples of concrete specimens were sampled during the first concrete placement (consisting of about 4150 m^3) and the foundation accomplishment (consisting of additional 1050 m^3).

Average compressive strength vales recorded at different concrete ages are reported in Table 7. Standard deviations values remained particularly low, clearly indicating the high homogeneity of the cast concrete.

Table 6. Final SCC mix composition

Constituents	Weight
Cement type CEM III/A class 32.5	340 kg/m^3
Mapeplast PZ300	50 kg/m^3
Filler VG1 Nicem	120 kg/m^3
Water	185 l/m^3
Sieved sand .0-4 mm	589 kg/m^3
Sieved sand 0-10 mm	455 kg/m^3
Coarse aggregates 8-16 mm	327 kg/m^3
Coarse Aggregate 11-22 mm	264 kg/m^3
Superplasticizer Dynamon SR 914	4.08 lt/m^3
Viscosity m.a. Viscostar 3k	0.50 lt/m^3

Table 7. SCC compressive strength evolution:
results from field sampled concrete specimens

Concrete age	Average Compressive strength (MPa)	Standard deviation (MPa)
3 days	19.2	2.43
7 days	32.1	2.53
14 days	41.0	3.01
28 days	47.7	3.21
90 days	59.9	3.29

Concerning thermal properties of the mixture, the temperature rise for the selected SCC mixture was calculated to be in the range of 29-30 °C. The result of the numerical calculation was compared with the experimental values recorded from a solid cubic meter of concrete cast as a test sample and instrumented with thermocouples. In particular, the concrete cube was built reproducing semi-adiabatic conditions, with thick thermal panels insulating all the cube sides. In this specific configurations, a maximum concrete temperature rise of 26 °C was measured at the age of 2 days from the cast. Such a performance was considered satisfactory and in good compliance with the specifications.

Graph in Figure 3 shows the temperature profiles recorded during the first 13 days after the concrete placement.

Blue line represents the temperature profile recorded at the maximum depth into the placement, at the foundation bottom, close to the ground (2.5 m below the final concrete top surface). These temperatures refers to the first layers of concrete placed into formwork.

Red line indicates temperature profile recorded at the middle depth of the placement (about 1.5 m below the final concrete level into formwork). From this we can observe the maximum concrete temperature remained any time quite lower than the required limit of 70 °C. On the other hand, the reached peak of temperature of about 58 °C was found to exceed the maximum experimental value recorded in (semi) adiabatic conditions on the concrete cube tested at the time of the concrete mixture qualification.

Green line refers to temperature data recorded at the cortical portions of the placement (at the depth of just few centimeters from the concrete free surface). The slope of the green profile is higher than in case of the red one, indicating that a faster temperature rise was experienced in this part of the mass concrete rather than in the middle thickness of the cast. This was considered to be a direct consequence of placing new layers of fresh concrete on top of already warm concrete represented by the previously cast part of the foundation. Actually, the same can be concluded also comparing temperature profile from the middle depth and the bottom side of the foundation respectively (red line in comparison with blue one).

Purple line represents the environmental temperature profile recorded during the concrete pour and after it.

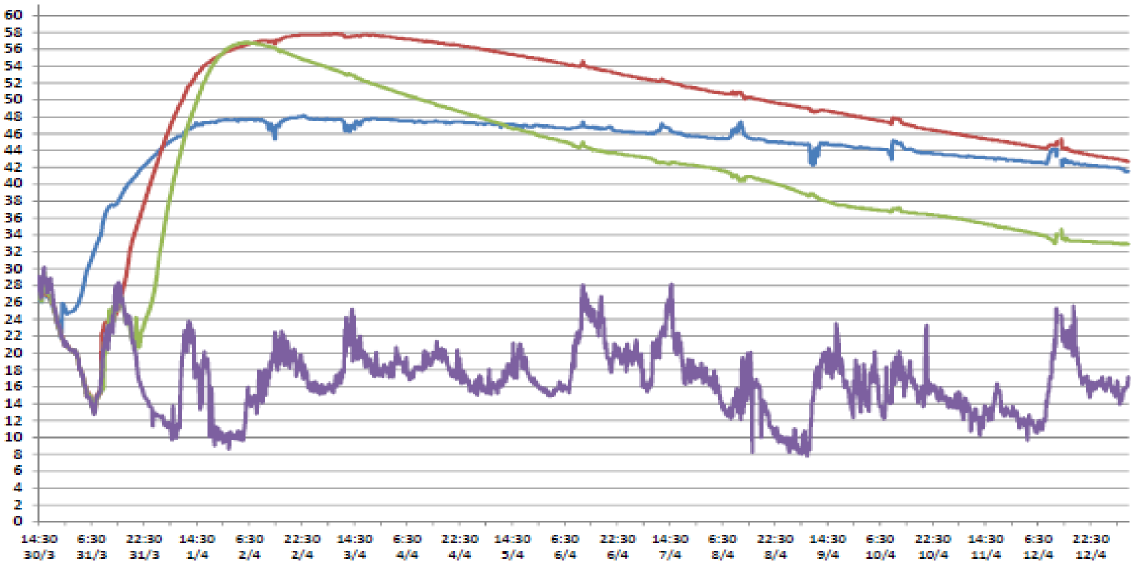

Figure 3. Concrete temperatures recorded during the first 14 days at different depths at the geometric center of the rectangular foundation.

From the graph it is possible to note that maximum cortical and core concrete temperature values were found to be very close to each other. Thermal profiles in Figure 3 also show that heat dissipation in the concrete mass took place at a relatively slow rate. Data clearly prove that temperature difference from part to part of the mass concrete never exceeded the specified limit of 20° C. In particular, the concrete surface and the core mass cooled about at the same rate, so that temperature difference remained almost constant and in the range of 8-10° C.

6 CONCLUSION

High performance concretes are experiencing a fast growing demand on the market, and their application is becoming frequent in case of massive cast and in high rise strategic structures. In all this application, improved mechanical properties are requested to modern concretes in combination to other special requirements also concerning rheology and control of heat release during concrete setting.

The present work presents the result of a research aiming to demonstrate feasibility of substituting relevant amount of cement with combination of secondary cementitious materials with no effect on the final compressive strength of the concrete. In particular, experimental tests have been carried out partially replacing cement dosage in reference concretes with ternary combinations (compounds) of calcareous filler, silica fume and grounded blast furnace slag and correspondent efficiency factors have been determined. In situ and experimental measurements confirmed the effectiveness of the selected compound in reducing cement dosages in concrete and controlling temperature rise during concrete setting in a large pouring of mass SCC concrete mix.

The method of selecting a premixed combination of secondary cementitious materials in place of handling single ingredients separately has been presented as an interesting possibility given to ready mixed concrete producers to reduce the number of the storage tanks in their plants. And, last but not least, reuse in concrete of byproducts such as silica fume and ground blast furnace slag is regarded as a positive example of green technology.

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