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Investigation of Thermal Properties of Cement Paste with Fluorescent Lamp Glass Waste, Glass Cullet and Coal/Wood Ashes

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The thermal character of cement hydration reactions causes concrete to endure temperature changes during the first days after casting. The present research intends to evaluate the influence on the temperature of hydration of cement paste mixes with local industrial wastes such as lamp glass waste powder/suspension, glass cullet, bottom/fly coal/wood ashes substitution at level of 20% and 30%. The temperature of hydration of cement paste mixes was investigated by using specially designed equipment. The temperature of hydration inside of the cement paste specimens was continuously monitored at least up to 20 h after production at ambient air temperature $20\pm2^{\circ}$ C. The results showed that cement paste substitution with lamp glass waste and coal/wood bottom ashes at level of 30% has influence on the peak temperatures of hydration with decrease from 58.8°C to 46.3°C and cement paste substitution with flint glass at level of 20% decrease temperature of hydration for around 19°C in comparison to control cement paste mix.

Keywords: thermal properties, fluorescent lamp glass waste, borosilicate lamp glass waste, glass cullet, ash.

1. Introduction

The world is facing an unprecedented challenge to reduce emissions of greenhouse gases, such as CO₂, to limit global warming and climate change. Cementitious materials, mainly concrete, have a big role to play in assuming a sustainable future. Every year about 1.5 m³ (3 tonnes) is produced for every person on the planet and this success is due to the widespread availability of the raw materials, its low cost and flexibility (Scrivener 2012). The reduction of energy consumption in construction and the solution of environmental problems by recycling of industrial and domestic waste is a relevant problem. Recycling is an important environmental and economical alternative for each material class, mainly for those that do not decompose easily in nature, such as glasses - not decomposed by microbial nor by atmospheric precipitation for thousand years (Delben et al. 2007). Finely ground glass waste having a particle size finer than 38 µm have pozzolanic behaviour and concrete containing ground glass exhibits a higher strength at both the early and late ages compared to fly ash concrete (Shao et al. 2000). Sahayan and Xu (2004) mentioned that fine glass powder could replace up to 30% of Portland cement. Within last decade most of research was carried out on utilization of glass waste in concrete as fine and coarse aggregates, mostly on mechanical properties of concrete, but only little research was carried out on the

thermal properties of such concretes (Poutos et al. 2008). Topcu and Canbaz (2004) concluded that when glass waste aggregates are used the workability of concrete is unaffected but the compressive, flexural and indirect tensile strength decrease in proportion to an increase in glass waste content. This finding is in general agreement with results obtained by Park et al. (2004). Improvements in cullet production methods were shown by Sangha et al. (2004) to produce concrete which was stronger than that made with natural aggregate in tension and compression when cement was replaced with glass cullet at levels of 60%. Significantly higher temperatures were generated during hydration of concrete made with glass aggregates than with natural aggregates; this trend was more marked with green glass than concrete made with amber or clear glass (Poutos et al. 2008). It was suggested by Poutos that if concrete made with glass aggregates is used for construction, there may be potential for two important applications, namely, cold weather concreting and for buildings to maintain greater temperature stability.

The hydration of a concrete mixture is a process that liberates heat and the rate of heat generation is accelerated with an increase in concrete temperature. Concrete is a poor conductor of heat, and the rate of heat evolution due to the hydration process is, therefore, much greater than the rate of heat dissipation. The development of high concrete temperatures causes a number of effects that show to be detrimental to long-term concrete performance. High concrete temperatures increase the rate of hydration, thermal stresses, the tendency for drying shrinkage cracking, permeability, and decrease long-term concrete strengths, and durability as a result of cracking. The higher the curing temperature is, the faster are the reactions between cement and water, and consequently the shorter becomes the setting time. Spontaneous dissolution of cement begins in the initial or preparatory phase, immediately after its contact with water. Small amounts of ettringite, calcium silicate hydrates (C-S-H) and calcium hydroxides (CH) are produced in the solid phase. This process lasts about 6 hours. In the second stage the formation of calcium silicate hydrate (C-S-H) continues. Calcium aluminate trisulphate hydrate, the so-called ettringite (Af_t), forms during the reaction of aluminium compounds in clinker with gypsum. The highest concentration of this hydrate is reached at the end of the second phase. This phase lasts from the 6th until the 24th hour. The processes that occur after 24 hours of hydration are called crystallization stage. In this stage Af, compounds react with the remaining clinker minerals and form calcium aluminate monosulpahte (Af_m) hydrates. C-S-H and CH content and crystal size increase. Hydration of clinker minerals are exothermic reactions and therefore a certain amount of heat is released when cement is mixed with water. The biggest amount of heat is released during the hydration of C₃A and C₃S, whereas C₂S reaction with water liberates very little heat (Taylor 1997). Heat liberation during cement curing has practical significance for concrete placing at low temperatures. On the other hand, big heat release has a negative impact in the manufacture of massive concrete structures. High temperature inside a massive structure and low temperature on the surface may cause the development of unfavorable stresses and cracking.

Specifications for temperature rise and differentials in massive pours require attention. A default peak temperature of 70°C is prudent as it would virtually eliminate the possible problem of delayed ettringite formation (DEF). While DEF is uncommon, it can cause enormous damage. Many specifiers focus on the temperature differential within the concrete mass and a value of 20 °C is often specified. However, in my experience which is primarily in temperate and tropical zones, most thermal cracking has been caused by external restraint of massive concrete elements by a rigid substrate during cooling. The attention on the differential temperature requirement in temperate conditions often leads to excessive insulation and increases both the peak temperature and the volume of concrete that reached high temperature. Therefore, to reduce a minor potential problem, the more likely problem is exacerbated. Many specifications limit concrete placement temperature to 32 °C or less. In massive elements, very high replacement levels of fly ash and GGBS are extremely useful to limit temperature rise. The elevated temperature means that the in-situ maturity is high at relatively early ages so that acceptable strength and penetrability properties do not take long to develop. There are many situations where in-situ maturity

monitoring can reduce unnecessary over-design of concrete mixes. An unnecessary impediment to sustainability and solving potentially serious thermal issues are the limits on supplementary cementing material replacement levels in many specifications. One does need to be cautious when using high replacement levels of fly ash in thin or suspended elements where the concrete could dry out and not develop the required properties. Well-meaning specifications which extend the compliance testing age for concrete specifically to enable high replacement levels without considering insitu development of strength and other properties can be problematic (Aldred, 2012).

There is no information about influence of fluorescent lamp glass waste on the temperature of hydration in cement paste and concrete. Therefore, in present study was investigated the influence of fluorescent lamp glass waste as cement component in cement paste mix on the temperature of hydration and for comparison were also investigated cement paste mixes substituted with bottom/fly ashes.

2. Methods

Ordinary Portland cement CEM I 42.5N was applied as a binding agent. Cement conforms to standard EVS EN 197-1:2002. Sikament 56 polycarboxylates plasticizing agent was added to several cement paste mixes.

Borosilicate (DRL) and fluorescent (LB) lamp glass waste powders that were obtained from lamp chippings were received from a local lamp recycling centre (Kara et al. 2012). Borosilicate glass is a type of glass with the main glass-forming constituents - silica and boron oxide. Borosilicate glass has a very low thermal expansion coefficient $(3.3 \times 10-6/K)$, about one-third that of ordinary glass and less dense than ordinary glass. The addition of lead oxide to glass raises its refractive index and lowers its working temperature and viscosity. The presence of lead is used in glasses absorbing gamma radiation and X-rays, used in radiation shielding (e.g. in cathode ray tubes, where lowering the exposure of the viewer to soft X-rays is of concern). The high ionic radius of the Pb2+ ion renders it highly immobile in the matrix and hinders the movement of other ions; lead glasses therefore have high electrical resistance, about two orders of magnitude higher than sodalime glass (108.5 vs 106.5 Ohm·cm, DC at 250°C). Leadcontaining glass is therefore frequently used in fluorescent light fixtures.

The fineness of powders was obtained by the Blaine apparatus Testing Bluhm&Feuerherdt GmbH (50ml) using a method with the prior need to prior measure of density of the powder with a pyknometer in accordance with EN 196-6. DRL lamp chippings were ground for 30 and 60 minutes to a Blaine fineness of 608 m²/kg and 746 m²/kg accordingly in laboratory planetary ball mill Retsch PM400 (with rotation speed 300 min⁻¹). LB lamp chippings were ground for 30 and 60 minutes to a Blaine fineness of 542 m²/kg and 576 m²/kg accordingly. Additionally, DRL lamp chippings were also ground for 60 minutes in water environment with water/glass (160/90) weight proportion in order to obtain glass waste suspension and improve fineness of particles (Kara, 2012). Glass cullet was obtained from the beer bottles (green, amber and flint colours) which were collected from the local glass bottle return point and manually crashed in the laboratory. Green, amber and flint glass chippings were ground for 30 minutes to a Blaine fineness of 460 m²/kg, 540 m²/kg and 500 m²/kg accordingly. Coal and wood bottom ash were obtained from local sources in Latvia. Coal bottom ash (CA) and wood bottom ash (WA) were ground for 30 minutes to a Blaine fineness of 849 m²/kg and 660 m²/kg accordingly. Coal & wood fly ash (FA) with Blaine fineness of 995 m²/kg was obtained outside from Latvia. The chemical composition of DRL, LB, coal/ wood bottom ashes and Portland cement is given in the table 1.

Table 1. The chemical composition of lamp glass waste, bottom ashes and Portland cement (Kara 2013)

Bulk oxide, % mass	DRL	LB	Wood ash	Coal ash	РС
CaO	1.320	5.110	13.5	20.42	67.01
BaO	1.63	2.362	0.13	0.21	0.04
Al ₂ O ₃	2.600	1,220	16.72	3.59	5.260
SiO ₂	71.140	55.04	49.69	59.93	18.74
K ₂ O	1.702	1.881	1.592	5.636	0.727
Na ₂ O	3.301	12.354	0.431	1.274	0.382
Fe ₂ O ₃	0.170	0.196	9.5	1.91	2.030
MnO	0.006	0.011	0.193	0.469	0.059
MgO	0.615	2.946	5.132	3.505	1.812
TiO ₂	0.006	0.027	0.84	0.193	0.261
SO ₃	0.045	0.264	0.552	0.024	3.004
P ₂ O ₅	0.023	0.038	0.865	1.723	0.151
B ₂ O ₃	16,63	0	0	0	0
PbO	0	18.30	0	0	0
Total	99.19	99.74	97.55	98.88	99.48

 Table 2. The cement paste compositions

The experimental programme to measure the temperature of hydration of cement paste mixes with lamp glass waste, glass cullet and ashes was divided in two sets. First set of experiments for lamp glass waste and ashes was hold at VGTU using following equipment (Fig. 1): cement paste mixes were cast in demountable 100·100·100 mm plywood moulds with a thermocouple (connected to a data transmitting device) polipropylene straw located in the center of one face of each mould. Four moulds were placed separately into four metal boxes with 30 mm thick insulation layer of polystyrene foam. Second set of experiments for glass cullet was hold at RTU using newly designed equipment with improved insulation, cement paste mixes were cast in demountable 150.150.150 mm plywood moulds with a thermocouple (connected to a data transmitting device) copper tube located in the center of one face of each mould. Four moulds all together were placed into one plywood box with 50mm insulation layer of Finnfoam (Fig. 1). The temperature was continuously monitored at least up to 20 h after production at ambient air temperature $20 \pm 1^{\circ}$ C.



Fig. 1. Equipment to measure hydration temperature inside of the concrete mixes: left at VGTU and right at RTU

In total, 34 cement paste mixes were prepared (table 2). However, w/c ratio strongly influence the hydration process, the purpose of the investigation was also to maintain the similar workability of the mixes (Kara 2013), therefore the w/c was not constant for all mixes. Portland cement was substituted at level of 20 and 30% with lamp glass waste.

Mix type	Grinding time, min	Cement replace- ment volume, %	W/C ratio	Portland cement CEM I 42,5 N, g	LB powder glass,g	DRL powder glass,g	DRL glass suspen- sion,g	Coal ash,g	Wood ash,g	Plasticizer,	Water, g
CTRL1	0	0	0.314	1000							314
LB1	30	20	0.314	800	200						314
LB2	30	30	0.314	700	300						314
DRL1	30	20	0.314	800		200					314
DRLS1	30	30	0.310	700			400				
CTRL2	0	0	0.273	1000						10	273
DRL2	30	20	0.273	800		200				10	273
LB3	30	20	0.273	800	200					10	273
CA1	30	30	0.285	700				300			285

Table 2 continuation.	. The cement _l	paste compositions
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Mix type	Grinding time, min	Cement replace- ment volume, %	W/C ratio	Portland cement CEM I 42,5 N, g	LB powder glass,g	DRL powder glass,g	DRL glass suspen- sion,g	Coal ash,g	Wood ash,g	Plasticizer,	Water, g
WA1	30	30	0.285	700					300		285
CWA1	30	30	0.285	700				150	150		285
FA1	0	30	0.360	700				Fly asl	n: 300		360
CTRL3	0	0	0.285	1000							285
CA2	30	30	0.243	700				300		10	243
WA2	30	30	0.243	700					300	10	243
CTRL4	0	0	0.243	1000						10	243
DRLCA1	30	30	0.261	700	300			90			285
LBCA1	30	30	0.261	700		300		90			285
DRLWA1	30	30	0.261	700	300				90		285
LBWA1	30	30	0.261	700		300			90		285
DRL3	60	30	0.285	700	300						285
LB4	60	30	0.285	700		300					285
DRLS2	60	30	0.285	700			585.5				
DRLLB1	60	30	0.285	700	150	150					285
DRL4	60	30	0.273	700	300					10	273
LB5	60	30	0.273	700		300				10	273
DRLLB2	60	30	0.230	700	150	150				10	230
CTRL5	0	0	0.285	3000							855
A1	30	20	0.285	2400	Amber glass, 600 g						
G1	30	20	0.285	2400	Green glass, 600 g						
F1	30	20	0.285	2400	Flint glass, 600 g						
A2	30	30	0.285	2100	Amber glass, 900 g						
G2	30	30	0.285	2100	Green glass, 900 g						855
F2	30	30	0.285	2100	Flint glass, 900 g						855

3. Results

Fig. 2 illustrates the relationship between temperature and time during the first 20 hours of hydration for LB1, LB2, DRL1, CTRL1 and DRLS1 mixes. The peak value of the temperature within the cement paste specimen was clearly defined and took place approximately 10 h after casting for all mixes. The highest temperature (67°C) achieved by CTRL1 occurred 9 h after casting. The generated temperatures during hydration of DRL1 and LB1 mixes were almost equal to CTRL1. The highest rise of temperature (59°C) for DRLS1 occurred 9 h after casting and showed lower result for almost 14% in comparison to CTRL1. The highest rise of temperature (68.4 °C) for DRL1 occurred 10 h after casting, for LB1 occurred 10 h after casting with value of 67.8 °C, for LB2 occurred 11 h after casting with value of 62.5 °C. The temperature of hydration of LB2 was for 8% lower than LB1.

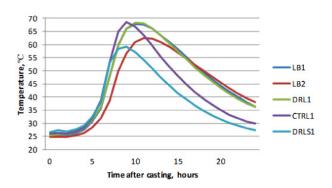


Fig. 2. Relationship between temperature and time during hydration for DRL/LB glass waste powder and DRL glass waste suspension cement paste mixes

Fig. 3 illustrates the relationship between temperature and time during the first 40 hours of hydration for DRL2, LB3 and CTRL2 mixes. The peak value of the temperature within the control cement paste specimen CTRL2 was clearly defined and took place approximately 17h after casting. The highest temperature achieved by CTRL2 was 79.4 °C.

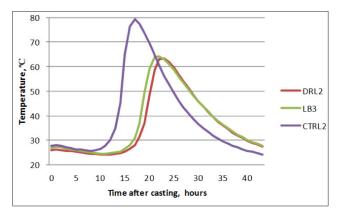


Fig. 3. Relationship between temperature and time during hydration for DRL and LB glass waste powder cement pastes with a plasticizing agent

The peak values of the temperature within the DRL2 and LB3 cement paste specimens were hindered and defined 23 h and 22 h after casting with values 63 °C and 64 °C correspondingly.

Fig. 4 illustrates the relationship between temperature and time during the first 20 hours of hydration for CA1, WA1, CWA1 and FA1 ash cement pastes and control cement paste CTRL3. The peak value of the temperature within the control cement paste specimen CTRL3 took place approximately 10 h after casting with value of 59 °C. The generated temperatures during hydration of cement pastes made with bottom coal ash CA1 (53°C) and bottom wood ash WA1 (55°C) were lower in comparison to CTRL3. The cement paste with mixed wood and coal bottom ashes content showed lower peak value of 46.6 m°C which is 21% lower than CTRL3 peak. The hydration of cement paste with coal/wood fly ash was hindered and peak was 16h after casting and was 52 m°C.

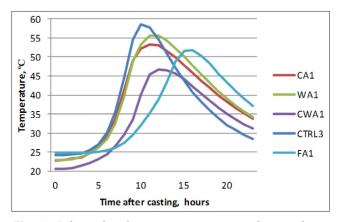


Fig. 4. Relationship between temperature and time during hydration for CA, WA, CWA and FA ash cement pastes

Fig. 5 illustrates the relationship between temperature and time during the first 40 hours of hydration for CA2 and WA2 ash cement pastes with plasticizing agent, FA1 ash cement paste without plasticizing agent and control specimen CTRL4. The peak value of the temperature within the control cement paste specimen CTRL4 took place approximately 14 h after casting with value of 64 °C. The generated temperatures during hydration of cement pastes made with bottom coal ash CA2 and bottom wood ash WA2 were lower in comparison to the control specimen CTRL4 with values of 52 m°C and 50 m°C correspondingly and hydration was also hindered for 10 hours in comparison to CTRL4. As it can be seen FA1 mix with the peak value of the temperature is reached almost by the same time as peak of CTRL4 and almost the same peak value of the temperature as for CA2 and WA2. The w/c ratio was higher for FA1 than for CA2 and WA2 due to the necessity of obtaining equal workability of the mixes.

Fig. 6 illustrates the relationship between temperature and time during the first 20 hours of hydration for DRL and LB glass waste powder cement pastes with WA and CA ashes and control specimen CTRL3. As it was mentioned above the peak value of the temperature within the control cement paste specimen CTRL3 took place approximately 10h after casting with value of 59 °C. It can be seen that hydration for all mixes was 12h after casting. Addition of WA into the mix with LB glass waste lowered hydration temperature in comparison to control mix for almost 19%.

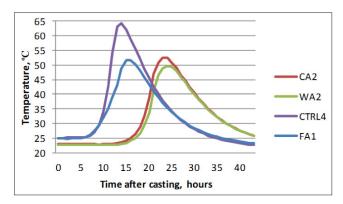


Fig. 5. Relationship between temperature and time during hydration for CA2 and WA2 ash cement pastes with a plasticizing agent, and FA1 ash cement paste without a plasticizing agent

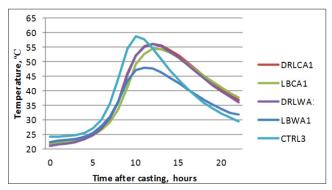


Fig. 6. Relationship between temperature and time during hydration for DRL and LB glass waste powder cement pastes with WA and CA ashes

Fig. 7 illustrates the relationship between temperature and time during the first 20 hours of hydration for DRL3, LB4, DRLS2, DRLLB1 and CTRL3. It can be seen that hydration temperature peaks took place within 10–13h after casting; significant difference in peak values in comparison to all mixes shown at fig.6 was only for DRLLB1 with peak temperature of 46.3 °C which is lower for 21.5% in comparison to CTRL3. Significant workability of the mix DRLLB1 in comparison to other mixes with the same w/c ratio was observed.

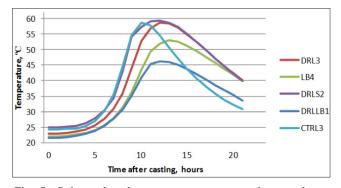


Fig. 7. Relationship between temperature and time during hydration for DRL and LB glass waste powder/DRL glass waste suspension cement pastes ground for 60 minutes

Fig. 8 illustrates the relationship between temperature and time during the first 40 hours of hydration for DRL4, LB5, DRLLB2 and CTRL2. It can be seen that hydration peaks for mixes DRL4, LB5, DRLLB2 took place within 20–25 h after casting and were also hindered for 9 hours in comparison to CTRL4. DRLLB2 had lower w/c ratio due to very good workability and equal temperature of hydration with DRL4. The best value of temperature of hydration was for mix LB5 (49.6 °C).

Fig. 9 illustrates the relationship between temperature and time during the first 20 hours of hydration for CTRL5, A1, G1 and F1. It can be seen that hydration temperature peaks for CTRL5 took place within 8h after casting with highest value of 93.6 °C.

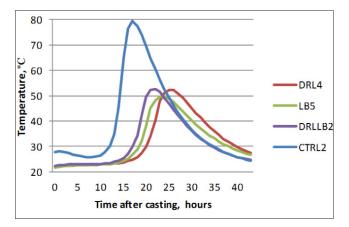


Fig. 8. Relationship between temperature and time during hydration for DRL and LB glass waste powder/DRL glass waste suspension cement pastes ground for 60 minutes with a plasticizing agent

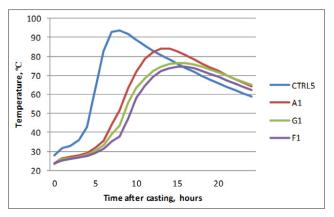


Fig. 9. Relationship between temperature and time during hydration for amber, green and flint glass waste powder cement pastes ground for 30 minutes

The hydration process of glass cullet cement pastes with 20% cement substitution was hindered for 5 hours in comparison to CTRL5 (Fig. 9). The highest value of the hydration temperature was for amber glass – 83,9°C and the lowest for flint glass – 74,4°C. Cement substitution with glass cullet at level of 30% didn't show so big difference for temperature of hydration among the amber, green and flint glass in comparison to cement substitution with 20% (Fig. 10). As it can be seen the hydration peaks have same values around 80°C which are lower for about 14°C in comparison to control mix CTRL5.

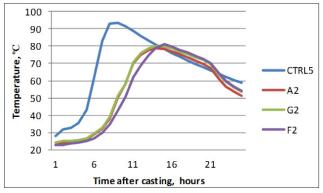


Fig. 10. Relationship between temperature and time during hydration for amber, green and flint glass waste powder cement pastes ground for 30 minutes

4. Discussion

The highest temperature rise and the greatest heat loss in cement paste occur during the first day of curing. Afterwards the transfer of heat slows down considerably and temperature rise in cement paste is insignificant. In the present study the maximum temperature during first day in cement paste was $68.4 \,^{\circ}$ C at ambient air temperature $20\pm1\,^{\circ}$ C, which is rather high and therefore Portland cement is not recommended for placing concrete in massive structures, for example. Properties like workability and temperature of hydration are developed through pozzolanic reaction between amorphous silica in the supplementary cementitious materials and Portlandite, (Ca(OH)₂), released during cement hydration and formation of insoluble calcium silicate hydrates (C-S-H) (Cook, 1986). The lamp glass waste and bottom ashes react pozzolanic to calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (C-A-H), and due to alkaline activation to aluminosilicate gels. The pozzolanic reaction of them is influenced by the reactivity and the interaction of different elements such as Si, Al, the alkalis and others. Particle size is influential in controlling the mechanism of pozzolanic reactions. The hydration of cement paste mix produces Ca(OH)₂ and it is consumed during pozzolanic reaction. Mixes composed of particles whose size is the smallest and surface area is the largest have the largest consumption of Ca(OH)₂. Dyer and Dhir (2001) concluded that increased Ca(OH), levels observed in glassbearing blends may be a result of glass constituents being incorporated into C-S-H in the place of Ca from the cement powder, resulting in excess Ca(OH), the pore solution.

It was observed that the cement substitution at level of 30% with glass waste ground for 60 minutes significantly influences on the workability of the mixes with low water absorption in comparison to the mixes with bottom ashes. Portland cement with substitution at level 30% with glass waste powder ground for 30 minutes showed slightly lower results in range of 2-3 °C difference in comparison to Portland cement control mix, and as far as glass waste was additionally was ground for 60 minutes in dry/water environment the peak temperatures were already lower up to 59 °C and for LB glass even 53 °C. The lowest peak temperature 46.3°C was for mix with DRL & LB glass waste (DRLLB1) and similar to the peak temperature 46.6 °C of mix CWA1 with Coal & Wood Bottom ashes. Somehow, mixes with two waste products like DRL & LB or CA & WA showed lower temperature peaks of hydration and performed better workability. It could be explained by the chemical composition of the combined waste materials. It was observed that the hydration temperature rises when cement substitution with green and flint glass increased up to 30%, except amber glass when temperature went down. Therefore, the optimal cement substitution with green and flint glass is at level of 20% with significant temperature of hydration for flint glass. It was observed that a plasticizing agent had slight effect on the temperature decrease in the range of 3-4°C.

5. Conclusions

Lamp glass waste, glass cullet and ashes have significant influence on the temperature of hydration in cement paste. Lower temperatures are generated during hydration of cement pastes (w/c = 0.285) substituted with lamp glass waste and bottom ash at level of 30%, and flint glass – at level of 20%. The temperature decrease from 58.8 °C to 46.3 °C is observed for cement paste mixes with lamp glass waste (DRLLB1) and from 58.8 °C to 46.6 °C for mixes with bottom ash (CWA1), and for flint glass from 93.6 °C to 74.4 °C. The cement paste mixes with glass waste ground for 60 minutes, flint glass ground for 30 minutes perform better workability, low water absorption in comparison to the mixes with bottom ash. It can be

concluded that the temperature rise declines as the quality of lamp glass waste improves: as finer are lamp glass waste particles (Blaine fineness above 600 kg/m²), less water is required to achieve the desired mix workability, lower is temperature of hydration of cement paste and higher is compressive strength.

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