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Noveltiesin Material Development for Massive Concrete Structures: Reduction in Heat of Hydration Observed in Ternary Replacement Mixtures

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Abstract: As the size of modern infrastructure increases, novelties related to mass concrete mixtures including supplementary cementitious materials (SCMs) become critical. The effects of binary and ternary cement replacement mixtures including metakaolin, silica fume, ground calcium carbonate, granulated blast furnace slag, and fly ash on the rate and amount of heat generated in concrete mixtures are investigated. Twenty three binary and ternary mixtures with a water-to-cementitious binder ratio of 0.43 are evaluated. Between 15% and 45% cement replacement by weight is considered. Results indicate that binary mixtures containing metakaolin or silica fume offer no advantage in reducing the amount of heat but increase compressive strength by 20%. On contrary, ternary mixtures, including two pozzolanic materials, provide 15% reduction in the amount of heat evolution without compromising strength. This reduction is observed regardless of alumina (Al) or silica (Si) content in pozzolanic materials when 45% cement is replaced with a combination of slag and metakaolin, or slag and silica fume. Furthermore, the effect of increased calcium (Ca) content is investigated. It is concluded that ternary mixtures with decreased Ca/(Al+Si) ratio reduce internal temperature in mass concrete structures and are less likely to be exposed to the threshold temperature for delayed ettringite formation.

Keywords: heat of hydration; ternary mixtures; binary mixtures; supplementary cementitious materials; mass concrete; cement replacement; metakaolin; silica fume; compressive strength; material development

1. Introduction

1.1. Background

Concrete is the material selected to build most of the world's infrastructure and used to provide reliable and modern infrastructure. The size of concrete structures, such as bridges, dams, foundations, and buildings, is rapidly increasing to carry greater loads and advance economic growth [1] although there is an opportunity to reduce such infrastructure in size with the advent of high performance concrete. Nonetheless, placements of mass concrete elements demand considerable control of temperature rise due to the heat of hydration of cementitious materials. Typical temperature rise in concrete mixtures ranges between 40 °C and 55 °C. Delayed ettringite formation (DEF) is a phenomenon in which the formation of mineral ettringite is delayed due to high early internal temperature in concrete. The ettringite formed during the initial stages of hydration is also decomposed in the event of elevated temperatures and may reform after the paste is already hardened. It usually occurs when the temperature exceeds 70 °C and causes expansion and cracking in concrete due to its large volume [2]. Therefore, an internal temperature rise in concrete structures can lead to DEF, undesirable thermal stresses, cracking, deleterious chemical reactions, or reduction in long-term strength [3]. Active cooling such as pre-cooling or post-cooling using pipe cooling systems [4] provides additional benefits in conjunction with the material development in controlling the temperature in mass concrete structures.

In this paper, novelties related to innovative combinations of supplementary cementitious materials (SCMs) for use in mass concrete placements are presented. SCMs enhance the overall properties of concrete and provide several engineering, economic and ecological benefits [5,6]. The examples of SCMs are fly ash (FA), metakaolin (MK), silica fume (SF), ground calcium carbonate (GCC), and granulated blast-furnace slag (GGBS) which is referred to as 'slag' or 'SL' hereafter. They represent a viable solution for partially substituting Portland cement [7–9]. Most widely used SCMs are fly ash and slag, with the annual global productions of approximately 990 million tons and 355 million tons, respectively [7,10]. They are often used to reduce the rate and amount of heat generation in mass concrete members. In this study, the potential for reducing the rate and amount of heat in binary and ternary replacement mixtures including SCMs is investigated, when limited supply of fly ash is available. In the U.S., limited material supply chain inventory related with the fly ash shortages had occurred for large infrastructure projects although the shortages vary by location. The circumstances surrounding the fly ash shortages caused construction professionals to look into alternative SCMs and new materials.

1.2. Literature Review

The hydration reaction of portland cement (PC) is exothermic, which means that heat is released from the reaction. The principal products from the cement hydration are calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) [11]. C-S-H is the main source of strength whereas the CH crystals are a source of weakness in cement paste matrix and have a "detrimental" effect on durability [8,11,12] since they are more soluble than C-S-H.

SCMs containing silica and/or alumina react with the excess CH in the presence of water. This reaction is referred to as a pozzolanic reaction and forms additional C-S-H and/or calcium aluminate hydrates (C-A-H) [8,11]. Therefore, partially replacing cement with SCMs enables CH consumption through a pozzolanic reaction which forms additional C-S-H and/or C-A-H. Such mixtures result in a strong cementation matrix which enhances durability [11]. Furthermore, a review of the literature indicates that binary and ternary replacement mixtures have the potential to reduce the rate and amount of heat [13–15].

The strength gained and the rate and amount of heat generated in a concrete mixture depend on pozzolans, cementitious content, water-to-cement (w/c) ratio, chemical compositions, and fineness, etc. This section focuses on presenting a literature review, which provides the effect of SCMs on the total amount of heat and compressive strength in binary and ternary replacement mixtures. However, it is important to recognize that the pore evolution inside concrete systems are very complex and thus is affected by multiple factors listed above. Furthermore, a layer of complexity is added when using a combination of different SCMs in ternary mixtures.

1.2.1. Effect of SCMs on Heat of Hydration

The effect of partially replacing cement with SCMs on the heat of hydration in binary mixtures is reported by several researchers. The authors of [16,17] reported that 15% MK replacement slightly reduced the early age heat of hydration up to 3 days although it is higher than the heat generated in the control mixture beyond the period. In these previous studies, a water-to-binder ratio of 0.45 is used. Previous findings are inconclusive on silica fume (SF). Partial replacements of cement by SF have reduced the heat of hydration [13,17,18], produced as much heat as the control mixture [14], or increased heat at certain replacement level (10%) and at later ages (10-day) [18]. In these studies on SF, a range of water-to-binder ratio between 0.25 and 0.45 is used. Slag is known to reduce heat of hydration, although it is often used at high replacement levels up to 75% [13,15,19–21]. Fly ash is well recognized to provide a slow rate of heat generation and thus is very effective in reducing the heat of hydration [13,14,16,22]. The heat of hydration in mixtures including GCC may increase or decrease [23,24], depending on the particle size of GCC. The rate of CH consumption in MK binary mixtures is reported to be higher than that of SF binary mixtures [22], followed by a relatively slower consumption rate in slag and fly ash mixtures [13,14,16,22].

Limited quantifiable data is available on the effect of SCMs in the ternary cement replacement mixtures on heat of hydration. Ternary mixtures prepared by partially replacing cement with a combination of fly ash and MK [16], fly ash and SF [14], fly ash and ground limestone [23], slag and MK [15], slag and SF [14], slag and ground limestone [21] indicate that the total heat energy may reduce in ternary mixtures.

1.2.2. Effect of SCMs on Compressive Strength

In binary mixtures, replacing cement by MK up to 20% has shown significant improvement in compressive strength development [22,25–28]. Similar to MK, partial replacements of cement with SF have also shown a substantial improvement in compressive strength when a 5% to 15% replacement is considered [28–31]. Slag, on the other hand, provides a slow rate of strength development but improves the 28-day and long-term compressive strength [27,32,33].

Similar to a literature search on the heat of hydration, limited studies have been performed to evaluate the effect of SCMs on compressive strength in ternary mixtures. When cement is replaced by a combination of slag and MK [26,27] or slag and SF [30], its early compressive strength is improved compared to a binary mixture containing only slag, as well as the 28-day strength. A range of water-to-binder ratio of 0.28 to 0.5 is used in these studies.

The optimum binary partial replacement levels considered for concrete mixtures containing SCMs in the literature are as follows: 10% to 20% in concrete mixtures including MK [16,17,22,25–28], 5% to 15% in the case of SF [13,17,18,28–30,34], 25% to 50% for slag mixtures [13–15,26,27,30,32,33], and 10% to 30% when GCC is used [21,23].

The cement replacement with SF or MK up to 15% is adequate in improving compressive strength and durability of concrete structures due to its extremely fine nature [11]. However, higher replacement levels beyond the optimum level (between 10% and 15%) results in reduced compressive strength [22,31] and increased heat of hydration (HoH) [16].

1.3. Scope and Objective

This study aims to answer important research questions and prove hypotheses true or false, which may eventually lead to a more accurate assumption or question. Therefore, the following three research questions and two hypotheses are considered:

1. Do binary replacement mixtures containing metakaolin, silica fume, or GCC reduce the heat of hydration?
2. Do ternary replacement mixtures containing slag and one of the above three materials reduce the total amount of heat?
3. If so, what is the optimum replacement fraction?
4. It is hypothesized that the strength gain from the exothermic pozzolanic reaction is associated with the total amount of heat gain in binary and ternary replacement mixtures.
5. It is also hypothesized that the combined amount of aluminate and silicate in pozzolans affects the heat generation.

This study focuses on obtaining the heat generated from cement hydration and pozzolanic reactions and determines the effect of binary and ternary replacement mixtures on heat of hydration. The main goal of this study is to identify SCMs that have the potential to reduce the maximum internal temperature in a mass concrete structure such that it is not exposed to 70 °C, which is the threshold temperature for DEF. This study is divided into 4 parts and investigates SCM replacement levels up to 45% by cement weight. The optimum replacement levels (e.g., 15%) obtained from the literature are selected for binary replacement mixtures.

In Part I, three concrete mixture groups are investigated to study the effect of cement content on the strength and workability. In Part II, two groups are selected in order to study the effect of binary and ternary replacement mixtures on the heat of hydration. Based on the findings of Parts I and II, the cement content is fixed at 422 kg/m^3 in Part III. Binary replacements of metakaolin (or silica fume) are considered, as well as ternary replacement mixtures containing slag/metakaolin or slag/silica fume. In the last part (Part IV), binary and ternary mixtures containing GCC and/or slag are investigated. The results are compared with the binary/ternary replacement mixtures including MK or SF. In this study, the term, 'heat of hydration (HoH),' is used to represent the total amount of heat liberated from each cementitious mixture. It indicates the total amount of heat generated from the hydration of cementitious materials including cement and pozzolans.

2. Materials and Methods

In total, 23 concrete mixtures are investigated in this study. Table 1 presents three mixture groups studied in Parts I through IV. The first part includes 13 mixtures to study the effect of cement content on compressive strength and workability. Three cementitious contents (specimen groups 422, 363, and 303) including slag, metakaolin, and fly ash are considered in this study as shown in Table 1 in order to examine the feasibility of reducing the heat generated from cement hydration and pozzolanic reactions. The second part includes 12 selected mixtures in 363 and 422 groups to study the effect of binary and ternary cement replacement mixtures including silica fume, metakaolin, slag, and fly ash on the heat of hydration (HoH). In this study, it is anticipated that the heat energy per gram of cementitious materials should be comparable between the two groups although the total HoH differs. The third part consists of 8 selected mixtures in the 422 group to further investigate the effect of binary and ternary mixtures on the heat of hydration and estimate the heat generated from the pozzolanic reaction(s). Finally, the last part (or Part IV) contains an additional 5 SCM mixtures in 422 group including GCC and other ternary replacement mixtures to further investigate variations in HoH identified in Part III.

Table 1. Mix proportion of the concrete mixtures, kg/m^3 (w/c = 0.43).

Mixture Designation (Group-Specimen ID)	Water Kg/m^3	Cementitious Content, kg/m^3						Sand Kg/m^3	Gravel Kg/m^3
		Cement	GCC	MK	SF	Slag	FA		
422-Control	181.5	422	0	0	0	0	0	717.6	984.4
422-MK15	181.5	358.7	0	63.3	0	0	0	717.6	984.4
422-SF15	181.5	358.7	0	0	63.3	0	0	717.6	984.4
422-GCC15	181.5	358.7	63.3	0	0	0	0	717.6	984.4
422-SL30	181.5	295.4	0	0	0	126.6	0	717.6	984.4
422-FA30	181.5	295.4	0	0	0	0	126.6	717.6	984.4
422-SL30+MK15	181.5	232.1	0	63.3	0	126.6	0	717.6	984.4
422-SL30+SF15	181.5	232.1	0	0	63.3	126.6	0	717.6	984.4
422-SL30+GCC15	181.5	232.1	63.3	0	0	126.6	0	717.6	984.4
422-SL35+MK10	181.5	232.1	0	42.2	0	147.7	0	717.6	984.4
422-SL40+MK5	181.5	232.1	0	21.1	0	168.8	0	717.6	984.4
422-SL45	181.5	232.1	0	0	0	189.9	0	717.6	984.4
422-FA45	181.5	232.1	0	0	0	0	189.9	717.6	984.4
363-Control	156	362.5	0	0	0	0	0	753.2	1034
363-MK15	156	308.3	0	54.4	0	0	0	753.2	1034
363-SF15	156	308.3	0	0	54.4	0	0	753.2	1034
363-SL30	156	253.8	0	0	0	108.8	0	753.2	1034
363-SL30+MK15	156	199.4	0	54.4	0	108.8	0	753.2	1034
363-SL30+SF15	156	199.4	0	0	54.4	108.8	0	753.2	1034
303-Control	130.7	303.2	0	0	0	0	0	789.8	1082.8
303-MK15	130.7	257.7	0	45.5	0	0	0	789.8	1082.8
303-SL30	130.7	212.2	0	0	0	91	0	789.8	1082.8
303-SL30+MK15	130.7	166.8	0	45.5	0	91	0	789.8	1082.8

2.1. Materials

Type I ordinary portland cement (OPC) with a specific gravity of 3.16 and a fineness of 387 m^2/kg is used. Table 2 provides the chemical composition and physical properties of the cementitious materials used in this study. These properties were supplied by their manufacturers. The coarse aggregate is no. 57 crushed rock per ASTM C33 [35] with a specific gravity of 2.65, and an absorption capacity of 0.49%. The fine aggregate per ASTM C33 [35] is used with a specific gravity of 2.65 and absorption capacity of 1.53%. The polycarboxylate ether (PCE)-based high-range water-reducing admixture (HRWRA) is used in all mixtures. A dosage of approximately 3.7 mL per kilogram of cementitious material is used in the 422 group mixture, where a dosage between 4.5 and 5.2 mL per kilogram of cementitious material is used in the 363 and 303 group mixtures.

Table 2. Chemical Composition and Physical Properties of the Materials.

Chemical Composition and Physical Properties	Cement	GCC	Metakaolin	Silica Fume	Slag	Fly Ash
SiO_2	19.7	-	50.75	95.61	33.33	49.27
Al_2O_3	4.7	-	45.91	0.208	13.5	20.9
Fe_2O_3	3	-	0.45	0.055	0.68	16.76
CaO	63.3	56.0	0.06	0.426	41.28	3.88
MgO	3.1	-	0	0.235	5.53	0.83
Na_2O	-	-	0.23	0.129	0.21	1.04
TiO_2	-	-	1.87	-	0.56	-
S	-	-	-	-	0.9	-
SO_3	3.2	-	0.08	-	2.3	1.87
CO_2	-	44.0	-	-	-	-
Loss on Ignition	2.7	-	0.42	2.11	-	1.65
Moisture Content	-	0.15	0.43	0.0251	-	0.13
Fineness, Amount retained on #325 Sieve, %	-	20	0	-	3	14.53
Specific Gravity	3.16	2.7	2.6	2.2	2.8	2.44
Blaine m^2/kg	387		14,200	22,920	472	-
C_3S	54%					
C_2S	15%					
C_3A	7%					
C_4AF	9%					

2.2. Mix Proportions and Mixture Designations

Table 1 presents the concrete material proportions for all mixtures. A water-to-cement ratio of 0.43 is maintained for all mixtures. The workability of each mixture is measured using the slump test prescribed by ASTM C143 [36]. The designation of each group and mixture is indicated by the group name followed by the cement replacement material and the percent weight replacement of cement. For example, '422-MK15' indicates a mixture in the 422 group with a 15% replacement of cement by metakaolin. '363-SL30+MK15' indicates a ternary mixture in the 363 group with a 30 and 15 percent replacement of cement by slag and metakaolin, respectively.

The mixtures were designed based on a mixture proportion commonly used for mass concrete placements by the Georgia Department of Transportation (GDOT) in U.S.A. The '422-control' mixture design presented in Table 1 is used for concrete placements of drilled shafts, as foundations for a highway bridge in Georgia.

2.3. Specimen Preparation

Concrete mixtures are prepared using a laboratory revolving drum mixer. Cylindrical specimens, 200 mm in height and 100 mm in diameter, are prepared in accordance with ASTM C192 [37] for compressive strength testing. The external mixing method per ASTM C1702 [38] is used to prepare isothermal calorimetry specimens (120 mL) for heat of hydration testing. In this study, the coarse/fine aggregate is screened out using a No. 5 sieve such that a mortar specimen is prepared consistent with the ASTM procedure.

2.4. Testing Methods

Cylindrical specimens are tested for compressive strength by a hydraulic press machine in accordance with ASTM C39/C39M [39] at a loading rate of 0.24 MPa/s. Three specimens were prepared for each test. The average strength of the 3 specimens at 1, 3, 7, and 28 days of age is reported. Isothermal calorimeter testing is conducted in accordance with the heat of hydration testing per ASTM C1702 [38]. In this method, the temperature of the calorimeter is maintained constant at 23 °C. The data (e.g., power and energy output of the samples) is collected for seven days.

3. Results

The test results from the control, binary, and ternary mixtures are presented in Figures 1–8.

3.1. Part I Results: Effect of Cement Content on Compressive Strength and Slump

The cement content was varied for two reasons: (1) to evaluate the workability when SCMs are used and (2) to evaluate the effectiveness of pozzolans with varying amount of CH available for a pozzolanic reaction. The compressive strength results of 13 mixtures are presented in Figure 1. The bar graph shows the 1, 3, 7, and 28-day compressive strength of each mixture. The increase in cementitious content (cement and SCMs) generally increased the compressive strength. As expected, the compressive strength of the 422 group's control mixture is higher than those of the 363 and 303 groups' control mixtures at all ages. The MK15 binary mixtures also showed consistent results among the three groups (422, 363, and 303). The 28-day strength of the MK15 mixture in the 422 group is approximately 3.5% and 2.2% higher than that observed in the 363 and 303 groups, respectively. The SL30 mixtures did not show a consistent trend. That is, the 363-SL30 mixture unexpectedly had the highest 28-day compressive strength. The compressive strength increased at all ages as the cementitious content in SL30+MK15 ternary replacement mixtures was increased, although the 28-day strength of the 363 group's SL30+MK15 mixture does not follow this trend.

The slump ranged between 50 mm and 200 mm for mixtures in 422 and 363 groups, whereas it consistently ranged between 0 mm and 40 mm for the mixtures in 303 group, despite of the fact that the maximum amount of HRWRA recommended by the manufacturer is used. Therefore, only 422 and 363 mixture groups were further studied for the heat of hydration evaluation shown in Part II.

3.2. Part II Results: Effect of Cement Content on HoH

The heat of hydration (HoH) results for 363 and 422 mixture groups are presented in Figure 2. Figures 3 and 4 include the thermal power curves of the two mixture groups, respectively. These curves represent the rate of heat generation and indicate the power needed to maintain the temperature of the calorimeter at 23 °C. As expected, the power curves between the two groups are similar because they represent the power per gram of cementitious materials in each mixture with the fixed water-to-cement ratio of 0.43. Based on the consistency and reliability of the results presented in this section and Section 3.1, the cement content of 422 kg/m^3 was selected for further investigation in Parts III and IV. Although the SCM/CH ratio is the same for both 422 and 363 group mixtures at a specific replacement level, the effect of the pozzolanic reaction is more pronounced with higher SCM and CH contents in the 422 group mixtures.

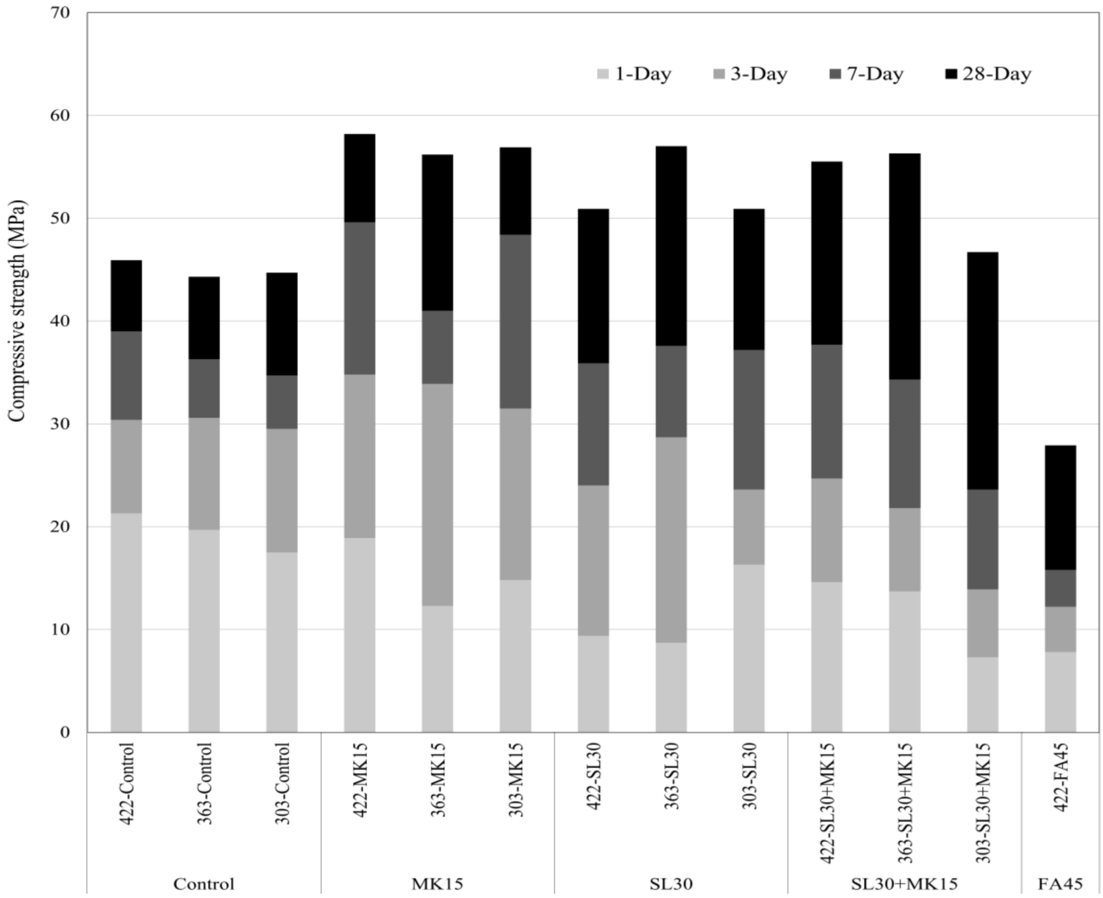

Figure 1. Compressive strength development of 422, 363, and 303 mixture groups.

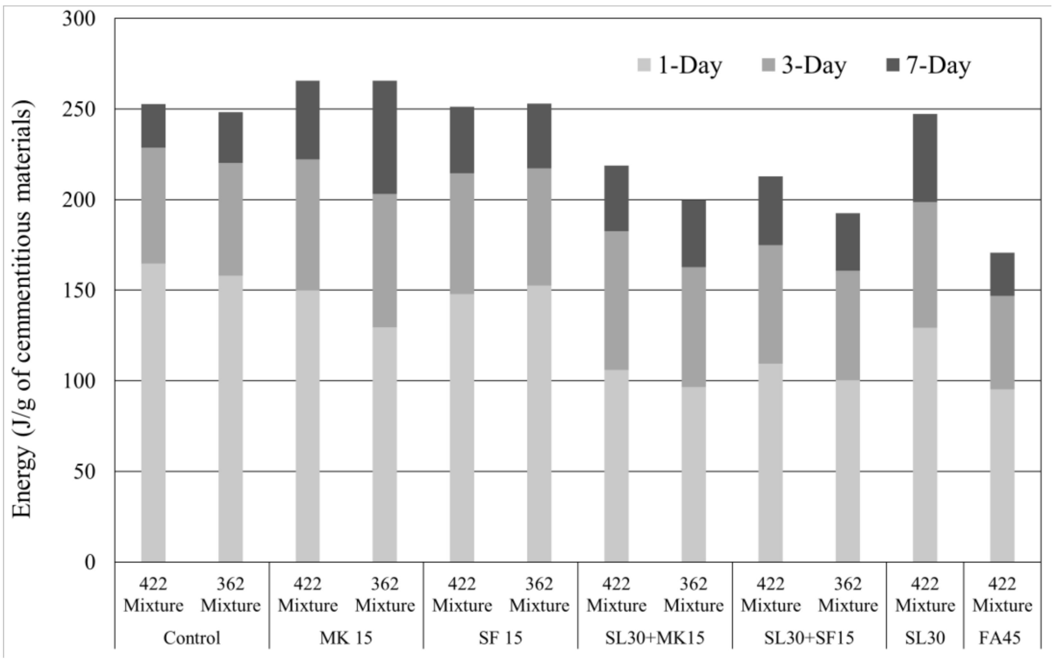

Figure 2. Heat of hydration of 422 and 363 mixture groups.

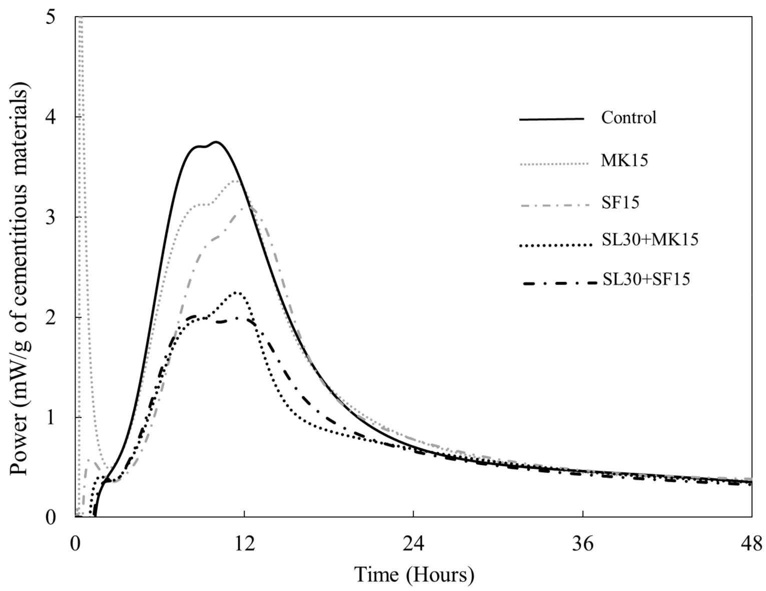

Figure 3. Rate of heat flow of 363 group mixtures.

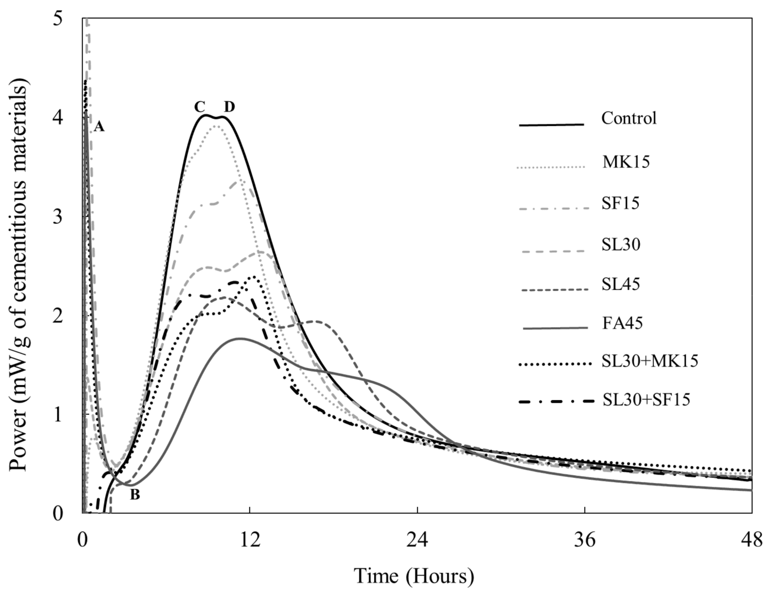

Figure 4. Rate of heat flow of 422 group mixtures.

3.3. Part III Results: Effect of Binary/Ternary Mixtures Including MK/SF on HoH and Strength in 422 Group

This third part presents the results of the 422 group mixtures. Figure 5 presents the HoH results of the 422 group mixtures only. It shows that binary replacement mixtures including MK, SF, and SL30 slightly reduce the 1-day and 3-day heat of hydration relative to the control mixture. However, after 7 days, the HoH of the MK mixture exceeds the control by about 5%, while the binary mixtures of both SF and SL30 generate similar heat energy to that of the control mixture. On the other hand, the 45% fly ash (class F) replacement mixture has a very slow rate of heat of hydration and significantly reduces the heat energy at all ages. The heat of hydration of the SL45 mixture is lower than the control at all ages, but it is higher than the FA45 mixture. A significant reduction in HoH is observed in ternary mixtures up to 7 days, as shown in Figure 5. The 1, 3, and 7-day heat of hydration is reduced by approximately 35%, 20%, and 13% in the ternary mixtures, 'SL30+MK15' and 'SL30+SF15', relative to the control mixture.

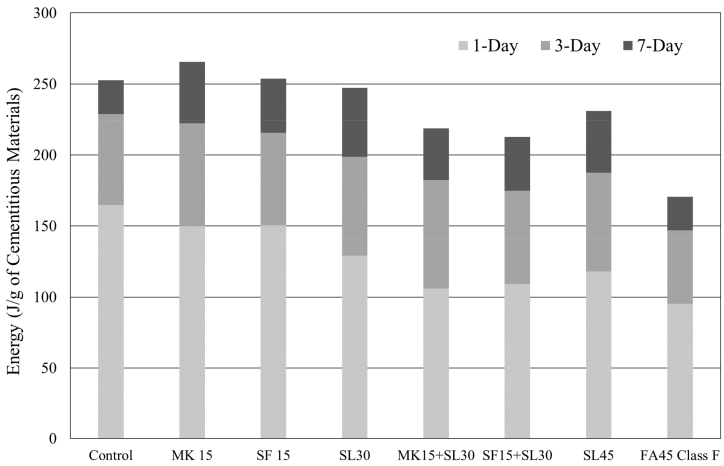

Figure 5. Heat of hydration of the 422 group mixtures.

Figure 4 shows that the rate of heat generation is reduced in binary mixtures, and this reduction is even more evident in ternary mixtures. The negative-valued endotherms on the heat flow curves result from early (<2 h) temperature acclamation of the specimens and do not affect the main hydration peaks. Point A represents the initial thermal power which is caused by rapid dissolution and initial hydration of the aluminate phase. Point B represents a dormant period associated with very low thermal power indicating slow and well-controlled hydration [40]. Point C represents the main hydration peak in the acceleration period which is mainly attributed to the silicate reaction and initiation of the strength generating alite or silicate hydration. Point D represents the accelerated calcium aluminate activity which is attributed to the second C_3A dissolution and results from the high exothermic dissolution of aluminate and continued formation of ettringite [40–42]. In the control mixture, the magnitude of point D is comparable to point C. However, in some binary and ternary mixtures, point D is located much higher than point C in the y-axis. This is due to the pozzolanic reaction between CH and SCMs [41,43].

Figure 6 presents the compressive strength development results of the 422 mixture group only. The performance of MK and SF is comparable in both binary and ternary mixtures in terms of both HoH and compressive strength development (Figures 5 and 6). Both MK and SF in binary mixtures provide comparable 1-day strength to the control mixture, and their strength become higher than the control mixture beyond this. The strength improvement in ternary mixtures containing MK or SF is observed. On the other hand, the HoH is reduced in ternary mixtures.

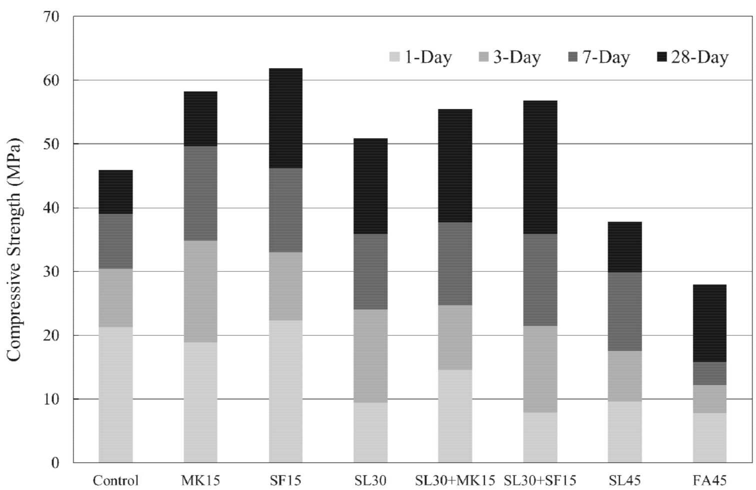

Figure 6. Compressive strength development of the 422 group mixtures.

3.4. Part IV Results: Effect of GCC and Other Mixtures on HoH

This fourth part is mainly designed to study the effect of increased calcium, Ca, content in ternary mixtures on HoH. Figure 7 presents the effect of GCC in binary and ternary mixtures and additional fly ash and slag mixtures on HoH. The results indicate the heat energy generated for a gram of cementitious materials in all of 422 group mixtures. It is shown that GCC15 is more effective in reducing the heat of hydration in binary mixtures compared to MK15 and SF15 mixtures. However, in ternary replacement mixtures, the 7-day HoH of the SL30+GCC15 is lower than the control mixture by 5%, but higher than the SL30+MK15 and SL30+SF15 by 10%.

Figure 8 shows the effect of ternary replacement mixtures containing various fractions of slag and MK on the heat of hydration. Among the replacement levels, SL30+MK15 offers the most reduction in heat energy recognizing that it is lower than that of the SL45 mixture. Table 3 presents the percent reduction in HoH in all of the 422 group mixtures over the control mixture at 1, 3, and 7-day of hydration.

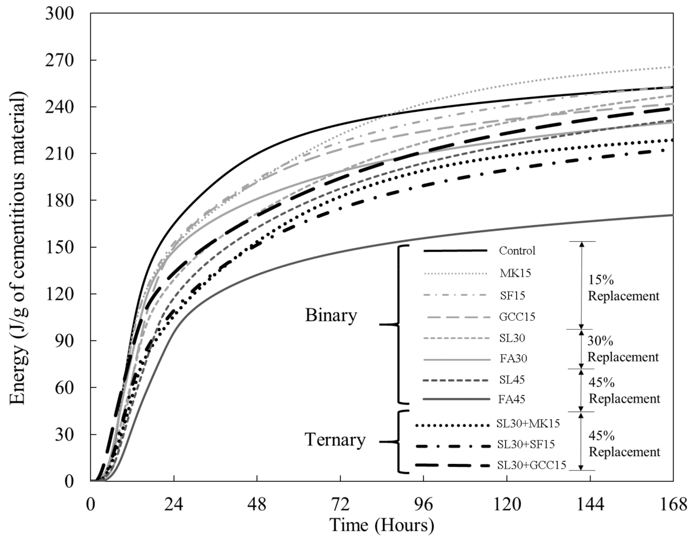

Figure 7. Heat of hydration of binary and ternary mixtures including ground calcium carbonate (GCC) in the 422 group.

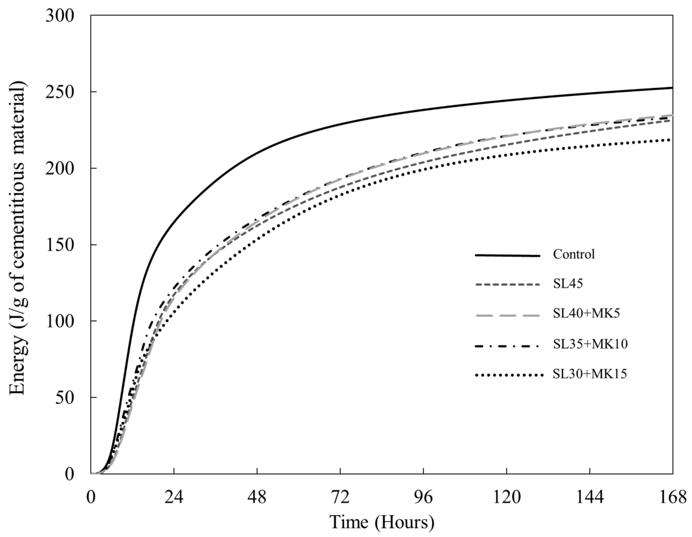

Figure 8. Heat of hydration of binary and ternary mixtures including slag (SL) and metakaolin (MK) in the 422 group.

Table 3. Percent reduction in heat of hydration in binary and ternary mixtures relative to the 422 control mixture.

Percent Cement Replacement (%)	Mixtures	Percent Reduction in HoH Relative to the Control Specimen		
		1 Day (%)	3 Day (%)	7 Day (%)
15	MK15	−9	−3	5
	SF15	−8	−6	0
	GCC15	−9	−7	−4
30	SL30	−22	−13	−2
	FA30	−11	−13	−9
45	SL45	−28	−18	−8
	SL40+MK5	−30	−16	−7
	SL35+MK10	−26	−16	−8
	SL30+MK15	−36	−20	−13
	SL30+SF15	−34	−23	−16
	SL30+GCC15	−19	−15	−5
	FA45 (class F)	−42	−36	−32

4. Analysis of Results

Based on the primary findings of the 422 group mixtures, the following analysis is made to study the effect of material types, binary/ternary replacement percentages, and ternary replacement fractions on HoH and compressive strength. Unless otherwise noted, the comparison of the results is made with respect to the control mixture in the 422 group.

4.1. Effect of Binary Mixtures on Compressive Strength

The 15% replacement of cement with MK provides a comparable 1-day compressive strength to that of the control mixture. It slightly reduces the 1-day strength by 11%, as shown in Figure 6. However, it increases the 3, 7, and 28-day compressive strength by 14%, 27%, and 27%, respectively. This result is consistent with the results found in the literature [22,25–28]. From these previous studies, the 10%, 15%, and 20% cement replacements with MK provided similar 1-day strength and increased 3-day and 28-day compressive strength by approximately 17% and 35%, respectively, when compared to the control mixture.

The 15% replacement of cement by silica fume (SF) results in 5%, 8%, 19%, and 35% strength gains on the 1, 3, 7, and 28-day, respectively, as shown in Figure 6. This finding is in agreement with the results obtained from literature [28–31], where a 10–15% cement replacement by SF increased the 3, 7, and 28-day compressive strength by approximately 4%, 22%, and 40%, respectively, when compared to the control mixture. The strength of the SF15 mixture is comparable to the MK15 mixture. This is also in agreement with a previous study [28]. This is due to their comparable fineness and surface area, as shown in Table 2. It is reasonable to expect the strength gains with the 15% of cement replacement with MK or SF due to their fine particle sizes and high silica and alumina content compared to Portland cement. These pozzolanic materials initially act as a filler until calcium hydroxide (CH) becomes available [7,25]. As the cement hydration continues, more CH becomes available and the pozzolanic reaction occurs. As a result of this reaction, additional calcium silicate hydrate (C-S-H) forms which provides additional strength.

The SL30 mixture provides a slow rate of strength development and reduces the 1, 3, and 7-day compressive strength by 56%, 21% and 8%, respectively. However, the 28-day strength increases by 11%. These results agree well with the results found in literature [27,32,33] including 22.5%, 40%, 45%, and 60% cement replacement with slag, in which slag decreased the 1, 3, and 7-day compressive strength by approximately 41%, 21%, and 13%, respectively, and increased the 28-day compressive by approximately 6%.

Partial replacement of 45% cement with slag or fly ash results in a very slow rate of strength development and significant reduction in compressive strength at all ages. The 28-day compressive strength of SL45 and FA45 binary mixtures are 17% and 39% lower than the control mixture, respectively.

This reduction in compressive strength is expected as a high percent (45%) of cement is replaced by slag or fly ash. Moreover, both slag and fly ash have a slow rate of heat generation as shown in Figure 4, which results in a slow rate of strength development. The FA45 has a slower rate of strength development than SL45, this is due to the lower rate of heat generation and pozzolanic reaction of the fly ash compare to slag, as shown in Figures 4–6.

4.2. Effect of Binary Replacement Mixtures Containing MK and SF on Heat of Hydration

In comparison with the control mixture, as shown in Figure 5 and Table 3, the 1 and 3-day heat of hydration is reduced by 9% and 3%, respectively, in MK15 mixture. The HoH is comparable to the control mixture by 84 h and exceeds by 5% at 7 days. This is in good agreement with the results found in the literature [16,17].

In case of SF15, the 1 and 3-day heat of hydration is reduced by about 8% and 6%, respectively, while it has a similar heat of hydration to that of the control mixture by 7 days. This result is consistent with the findings obtained from the literature [13,14,17,18]. In those previous studies, the 1, 3, and 7-day heat of hydration was reduced by approximately 12%, 10%, and 5%, respectively, when 10%, 15%, 20%, 30%, and 40% cement was replaced by SF. It is concluded that no significant change in HoH is observed in the binary mixtures based on Figure 5 and Table 3. The heat of cement hydration is reduced by removing 15% of the Portland cement by weight; however, there is no significant change in the total amount heat due to the exothermic pozzolanic reaction.

4.3. Effect of Binary Mixtures Containing Fly Ash and Slag on Heat of Hydration

FA30 reduces the 1, 3, and 7-day heat of hydration by 11%, 13%, and 9%, respectively. Meanwhile, SL30 mixture reduces the 1, 3, and 7-day heat of hydration by 22%, 13%, and 2%, respectively. This result agrees well with the previous findings [13,15,21], in which the 3- and 7-day heat of hydration was reduced by approximately 15% and 3%, respectively, when 20% to 55% of cement was replaced by slag.

As anticipated, FA45 significantly reduces the heat of hydration at all ages, and its 1, 3, and 7-day heat of hydration is 42%, 36%, and 32% lower than the control mixture, respectively. The slow rate of heat generation in the FA mixture is attributed to the relatively low specific surface area and the low solubility of the alumino-silicate glass in the alkaline environment of the PC hydration [16]. On the other hand, the HoH in SL45 is significantly higher than FA45 although it is slightly lower than that of the SL30 mixture, as shown in Figure 7.

Table 2 shows that the slag is finer than the fly ash. Therefore, the fine particles of the slag react more quickly than the large particles of fly ash. The slag also has a higher CaO content compared to the fly ash. These factors result in a higher heat generation in the slag mixtures when compared to the fly ash mixtures.

4.4. Effect of Binary GCC Mixture on Heat of Hydration

GCC15 reduces the 1, 3, and 7-day heat of hydration by 9%, 7%, and 4%, respectively. This is in good agreement with the available results [23], where the 15% limestone reduced the 2-day heat of hydration by 8%. Ground calcium carbonate (or GCC) is not a pozzolanic material, and hence it does not generate heat when used as partial replacement of cement. Therefore, the reduction in heat of hydration in GCC15 mixture is mainly attributed to the reduced amount of cement.

4.5. Effect of Ternary Mixtures on Heat of Hydration

4.5.1. Identification of Optimum SL and MK Fraction in 45% Replacement Ternary Mixtures

Current study employs 45% cement replacement mixtures. The replacement fraction in the ternary mixtures is determined by studying the heat of hydration in the following mixtures: SL45, SL30+MK15, SL35+MK10, and SL40+MK5. It was anticipated that SL45 would result in the least HoH since other mixtures contain MK, which provides a higher pozzolanic capacity/activity than slag [11]. Contrary to this expectation, the SL30+MK15 mixture leads to the least heat of hydration as shown in Figure 8. These results show that the optimum weight fraction of pozzolans used in ternary replacement mixtures is 2:1 (slag:metakaolin), when a 45% ternary replacement is considered. The same replacement levels are selected for SL30+SF15 and SL30+GCC15 ternary replacement mixtures. The 15% replacement level was optimum for binary mixtures including MK, SF, and GCC based on the literature.

4.5.2. Analysis of Heat of Hydration Results in Ternary Mixtures

Based on the results of Section 4.5.1, ternary replacement mixtures including 30% slag and 15% MK, 30% slag and 15% SF, or 30% slag and 15% GCC are studied. These three mixtures include an increased amount of Al, Si, and Ca, respectively. In this study, SL30+MK15 reduces the 1, 3, and 7-day heat of hydration by 36%, 20%, and 13%, respectively, compared to the control mixture of the 422 group. This is in agreement with the previous study [15] conducted by Boháč et al., where the 3-day heat of hydration was reduced by about 60% in SL30+MK5 mixture. Despite of the reduced cement replacement in the SL40+MK15 mixture (from 35% to 55%), the 3-day heat of hydration is unexpectedly increased by 27% from the SL30+MK5 mixture. The percentage of SiO_2 and Al_2O_3 in their MK was 57.3 and 38.6, respectively, whereas in this study, 50.8% (SiO_2) and 45.9% (Al_2O_3) are used. It is anticipated based on the previous study that additional alumina content may confer different heat releases. Therefore, the results of SL30+SF15 are analyzed to study the effect of increased silica content. In this ternary mixture, MK15 from the 'SL30+MK15' mixture is replaced with SF15 (with 95.6% silica content).

In case of the 'SL30+SF15' mixture, the 1, 3, and 7-day heat of hydration is also reduced by 34%, 23%, and 16%, respectively. This result is consistent with available literature [14], where the SL30+SF32.5 mixture reduced the 3-day heat of hydration by 17%. At a higher replacement level of SL47.5+SF32.5, the 3-day heat was reduced by about 41%. Limited information was found in the literature regarding the reduction in HoH in ternary replacement mixtures including slag and silica fume.

Both ternary mixtures include aluminate, possibly sufficient amount for the calcium aluminate sulfate (AFt or ettringite) formation. When pozzolans contain aluminate, AFt phases can form during the pozzolanic reaction. Moreover, both ternary mixtures have high silicate which results in the formation of additional C-S-H. The aluminate hydration reacts with CSH and releases calcium carbonate which is known to convert AFt phase to monocarbonate. Boháč's study [15] indicates that little to no AFt is found in ternary mixtures including SL and MK, whereas it was found in binary mixtures including MK. The presence of water-rich AFt increases the total volume of hydration products, and thus the total amount of heat is relatively lower in ternary mixtures due to the absence of AFt. The total heat energy in the 'SL30+SF15' mixture is similar to the 'SL30+MK15' mixture. Therefore, the heat of hydration reduces at all ages regardless of increased alumina or silica content in ternary mixtures. However, the combined alumina and silica content appears to affect the total amount of heat. Furthermore, the calcium carbonate ($CaCO_3$) content (or cement replacement level) should affect the HoH. Therefore, the results of SL30+GCC15 are analyzed to study the effect of increased 'Ca' content. In this ternary mixture, SF15 is replaced with GCC15 (with 95% $CaCO_3$ content).

In the 'SL30+GCC15' mixture, the 1, 3, and 7-day heat of hydration is reduced by 19%, 15%, and 5%, respectively. This outcome is in agreement with previous findings [21]. In the previous study, SL27.5+Limestone12.7 and SL37.3+Limestone12.7 mixtures, prepared by volumetrically replacing cement with these materials, reduced the 3-day heat of hydration by 7% and 17%, respectively. In this study, the increased Ca content appears to increase the HoH relative to the two ternary mixtures, 'SL30+MK15' and 'SL30+SF15'.

It is concluded from the findings presented in this section that the presence of two pozzolanic materials including high alumina and silica contents in ternary replacement mixtures result in reduced heat release, as well as adequate strength development as discussed in the following section. Based on the findings of the three ternary mixtures, the Ca/Al, Ca/Si, and Ca/(Al + Si) ratios are evaluated as presented in Table 4. It is concluded from this table that the amount of heat is proportional to the Ca/(Al + Si) ratio.

Table 4. Oxide ratios for select 45% replacements.

Mixtures	Ca/AL	Ca/Si	Ca/(AL + Si)
Control	13.5	3.2	2.6
SL45	6.2	2.1	1.6
FA45	3.1	1.1	0.8
SL40+MK5	5.0	1.9	1.4
SL35+MK10	4.1	1.8	1.3
SL30+MK15	3.49	1.7	1.1
SL30+SF15	7.1	1.3	1.1
SL30+GCC15	8.4	2.7	2.0

4.6. Effect of Ternary Mixtures on Compressive Strength

Replacing 45% cement with SL30+MK15 reduces the 1-day strength by 31%, however, it provides comparable 3 and 7-day strength to the control mixture, and its 28-day compressive strength is 21% higher than that of the control mixture. This agrees with previous studies [26,27], where the 7-day strength of the SL+MK mixture was comparable to the control mixture, and the 28-day compressive strength increased by approximately 39%. In the previous studies, 40% of cement was replaced by slag and MK in mixtures of SL30+MK10 and SL20+MK20.

In case of SL30+SF15, the 1 and 3-day compressive strength has decreased by 63% and 29%, respectively, while it has a comparable 7-day strength to the control mixture and its 28-day compressive strength is higher than the control mixture by 24%. This result is in agreement with the literature [30], in which SL35+SF10 reduced the 3-day compressive strength by 25%, but increased the 28-day compressive strength by approximately 12% relative to the control mixture.

The compressive strength of the SL30+MK15 is significantly higher than the SL45 and FA45 at all ages, and its 1, 3, and 28-day strength is 87% to 100% higher than the FA45. The inclusion of 15% MK into the slag mixture leads to the increased early-strength development and improves the strength of the slag mixtures at all ages, while significantly reducing the heat of hydration.

On the other hand, the SL30+SF15 mixture has a similar 1-day compressive strength to the SL45 mixture, however, its 3- and 28-day strength is 22% and 48% higher than SL45 mixture, respectively. Similar to the MK, the inclusion of 15% SF into the slag mixture improves the strength of the slag mixtures at all ages. With the strength gain and the formation of C-S-H and C-A-H, an increase in the total amount of heat is expected; however, a reduction in the heat of hydration is observed.

4.7. Estimating the Heat Generated from Pozzolanic Materials

In order to isolate the heat energy released from the pozzolanic reactions, the heat released solely from cement hydration in each binary and ternary mixtures is estimated by linearly extrapolating the HoH obtained from the control mixture as shown in Figure 9. The heat generated from the pozzolanic reaction in each mixture is then estimated by deducting the heat release due to cement hydration in Figure 9 from the total heat of hydration of each mixture shown in Figure 10. The same approach for separating the HoH of slag from portland cement in blended mixtures is used by [44,45]. Figure 11 shows the estimated heat release solely from the presence of the pozzolanic materials in each mixture. The shape and slope of the curves is considered to indicate the rate of pozzolanic reaction. It should be recognized in reviewing Figure 11 that a comparison should only be made between mixtures of the same cement replacement levels. For instance, a fair comparison is made between the 45% replacement mixtures (SL45 and SL30+MK15).

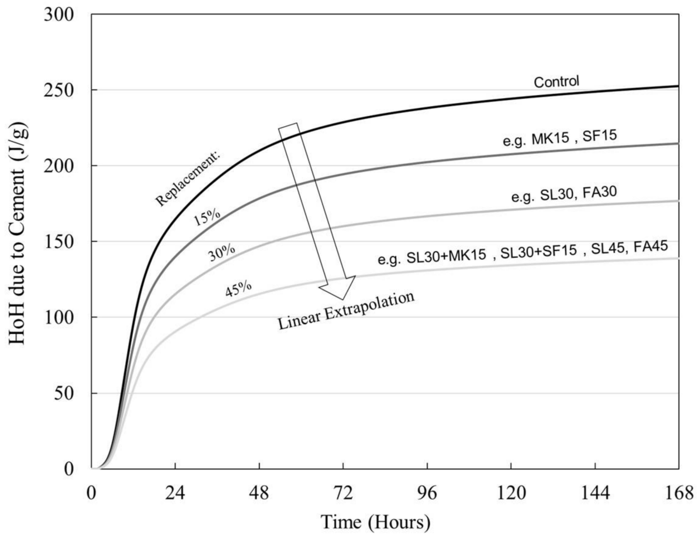

Figure 9. Linear extrapolation of the heat of hydration of the control mixture.

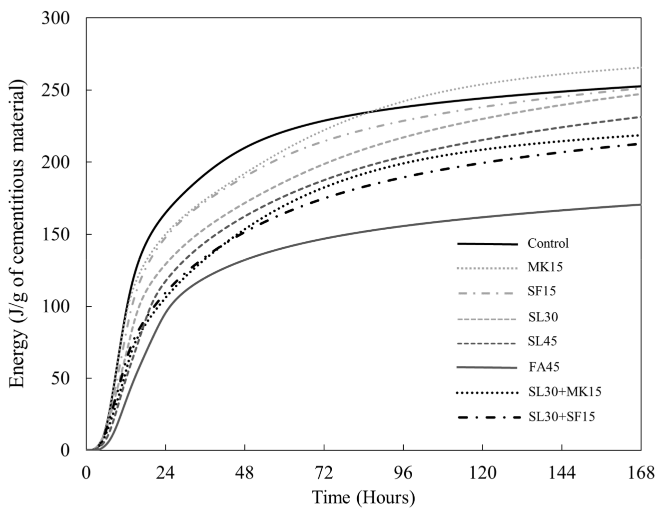

Figure 10. Heat of hydration of the 422 group mixtures to generate pozzolanic reaction.

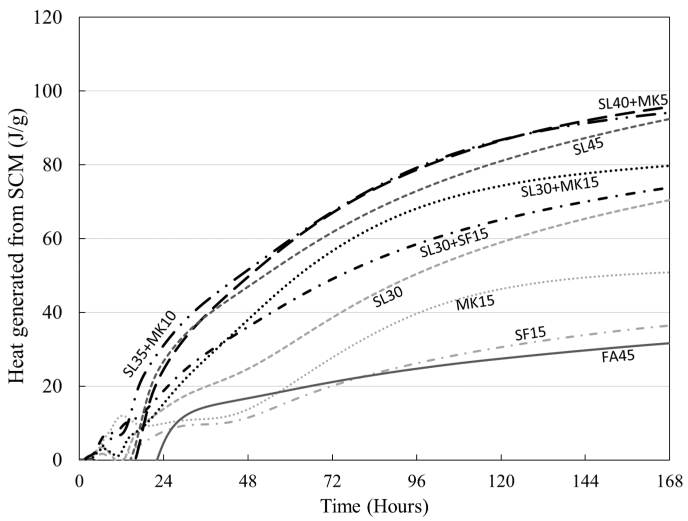

Figure 11. Heat of hydration generated from the pozzolanic reaction.

4.7.1. Estimated HoH in Binary Mixtures Including MK or SF

Figure 11 shows that the pozzolanic reaction of the binary mixtures (MK15 and SF15) starts after 2 days, and the pozzolanic reaction mainly occurs between 2 and 5 days. The rate of heat release is slightly higher in the MK mixtures than that of the SF mixtures up to 7 days. This may be attributed to the chemical composition of the two materials, as the MK contains higher alumina content which accelerates the pozzolanic reaction [46]. The higher initial reactivity of MK is attributed to its Al_2O_3 phases [22], which are involved in the formation of aluminium-hydrated compounds, C_2ASH_8 (gehlenite) and a small amount of crystalline C_4AH_{13} phase, when react with CH [47]. In the 'MK15' mixture shown in Figure 11, the heat release reaches a plateau at 7 days which indicates that the initial calcium hydroxide produced from cement hydration has been mostly depleted within a week [11]. On the other hand, the shape of the SF15 curve shows that the pozzolanic reaction lasts beyond 7 days and that the heat release gradually occurs. This rate of heat generation in both mixtures (MK15 and SF15) is consistent with their compressive strength development shown in Figure 6. In the MK15 mixture, the rate of strength development is the highest between 1 and 7 days. On the other hand, this rate in SF15 mixture is the highest between 7 and 28 days. The crystallization degree of the SCM is directly related to the SCM/lime reactivity. Metakaolin and silica fume exhibit low crystallization degree that leads to a high reactivity with lime, whereas fly ash has a higher degree. Thus, longer reaction time is required for fly ash.

4.7.2. Estimated HoH in Other Mixtures

In Figure 11, SL35+MK10 and SL40+MK5 have the highest rate of pozzolanic reaction among the 45% replacement levels followed by SL45 mixture. On the other hand, the FA45 mixture shows a very slow rate of heat release (or pozzolanic reaction over time). This is consistent with the compressive strength development of this mixture which is developed very slowly over time. The rate of heat evolution from the pozzolanic materials of SL30+MK15 and SL30+SF15 mixtures is similar, but the amount of heat is reduced by 15% over the control mixture. This reduction in HoH may be attributed to limited amount of calcium hydroxide (CH) formed in the ternary mixtures. That is, 2 pozzolanic materials may compete for CH. This deprivation may result in a relatively slow rate of HoH and total cumulative heat release. The reduction in HoH is not fully explained by the CH content alone but appears to be correlated with the Ca/(Al + Si) ratio.

5. Discussion and Future Work

The answers to the three research questions and two hypotheses, presented in Section 1.3, are provided in this section:

5.1. Answers to the Research Questions

- Binary mixtures containing metakaolin, silica fume, or GCC do not significantly reduce the heat of hydration.
- Ternary replacement mixtures containing slag and one of the above three materials significantly reduce the total heat of hydration.
- The optimum replacement weight fraction for ternary mixtures including SL and MK is 2:1 (SL:MK), when a 45% cement replacement is considered.

5.2. Answers to the Research Hypotheses

- In binary mixtures, the strength gain from pozzolanic reaction is correlated to the total amount of heat gain. However, this does not hold true in ternary replacement mixtures where the heat release is unexpectedly reduced inconsistent with the strength development.

- The total aluminate content in pozzolans such as slag and metakaolin affects the total amount of heat generation in ternary mixtures. However, it appears that the silica content also affects the total amount of heat.

5.3. Future Work

Placements of large concrete structures demand considerable control of temperature rise due to the heat of hydration. Supplementary cementitious materials provide significant long-term benefits and have the potential to prevent DEF, undesirable thermal cracking, deleterious chemical reactions, and reduction in long-term strength. It is also recommended that the concrete research community look into other innovative materials such as barium hydroxide, a phase-changing material, and poly vinyl acetate which is commonly found in paint products and thus economical. In addition to SCMs, these polymer modified and phase-changing materials may have a high potential to reduce the heat of hydration.

Based on the findings of this study, the ternary replacement mixtures (SL30+MK15 or SL30+SF15) reduce the total amount and rate of heat in mass concrete placements. However, varying cement replacement levels should be studied for ternary mixtures including slag and silica fume in the future. Specifically, the reduction in heat of hydration at higher replacement levels of slag needs to be evaluated. The mechanical performance of the concrete at early ages (up to 12 h) may be evaluated as the SCMs could present high activity. The amount of calcium hydroxide and its rate of consumption in binary and ternary replacement mixtures needs to be quantified. The relationship between heat of hydration and pozzolanic activity (e.g., CH consumption) should also be studied. Finally, X-ray diffraction and scanning electron microscope tests are recommended for ternary mixtures, in conjunction with the previous study conducted by Boháč et al. [15].

6. Conclusions

The effects of binary and ternary mixtures, including metakaolin, silica fume, GCC, and slag, on the heat of hydration are investigated in this study. Under the test conditions reported herein, the following conclusions are made:

- Binary replacement mixtures containing a pozzolanic material such as metakaolin (15%) or silica fume (15%) offer no significant advantage in reducing the heat of hydration, although the compressive strength increases by more than 20% on 28th day. As anticipated, binary replacement mixtures containing a non-pozzolanic material (15% GCC) results in a slight reduction in heat of hydration (4%) over a 7-day period.
- The optimum weight fraction of pozzolans used in ternary replacement mixtures is 2:1 (slag:metakaolin), when a 45% ternary replacement is considered.
- In binary mixtures, the rate of heat evolution is consistent with the strength development. However, in ternary mixtures including 30%SL and 15%MK or 15%SF replacements, the strength development is not consistent with the rate of heat evolution.
- The presence of two pozzolanic materials including high silica and alumina contents in ternary replacement mixtures results in approximately 15% reduction in the total amount of heat within 7 days and 11% strength gain by 28 days, relative to the control mixture. The amount of heat generated in ternary mixtures is proportional to the Ca/(Al + Si) ratio.
- Binary replacement mixtures containing 45% cement replacement by fly ash and slag (FA45 and SL45) reduce the heat of hydration by 36% and 13% by 3 days, respectively, when compared to the control mixture. The difference in the total amount of heat between ternary mixtures (SL30+MK15 or SL30+SF15) and FA45 is approximately 14% and 17% by 3 and 7 days after concrete placement, respectively.

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