Experimental Comparative Study of Effect of Different Additive Materials on Concrete Mix Alkalinity and Heat Generation

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Abstract. There are different methods to minimize the evolution of heat in concrete. Since the cement is the main component that generates heat, the first procedure may be to reduce its quantities by replacing cement with fine materials that do not release heat during its reaction. This paper studies the influence of different additives (fly ash, silica fume, and metakaolin) to the concrete mixture with different ratios of (0, 5, 10, 15, 20, 25, 30%) by weight of cement, with different parameters study, were presented, including impact of additives on (compressive strength, alkalinity, heat of hydration with fixed w/c ratio of 0.35, initial setting time, final setting time and impact of w/c ratio on heat of hydration with three w/c ratio of (0.3, 0.35 and 0.4)). The water cementations materials ratio was kept steady at (0.35). The heat of hydration measurement was carried out under isothermal constrain(25±0.1°C). Thermocouples were utilized to evaluate the heat of hydration of concrete by stating time from 0 to 24 hours and measured by a thermoelectric device. Concrete cubes with dimensions 100x100x100 mm for compressive strength test were used and examined at the time of 28 days, using different mix proportions resulted from different percentages of cement additives, to perform the compressive strength test. The results revealed that the Portland cement heat of hydration is retarded in the presence of additives. The decrease in pH of the concrete mix before casting and molding affects the early hydration and strength but improves the later age concrete properties.

1. Introduction
The main factors affecting concrete are cement formation, water-cement ratio, time of curing and processing temperature when ordinary Portland cement is mixed with water; a series of chemical reactions begin to occur. Cement has become an uncommon resource worldwide due to its increasing demand. Construction activities have increased in almost all developing countries in the world. Considerable work has always been performed to enhance the quality and standards of concrete properties as building materials [1-3].

Concrete is considered one of the most used building materials due to its good strength compared to cost. Concrete durability is a major concern in civilian structures because it relies heavily on material interactions with the environment. Reducing the pH of the concrete due to carbonation does not cause corrosion, but also causes the chloride to penetrate. Chloride prevalence depends on many factors (w/c ratio, type, mineral additive, and cement ratio, etc.), densification, curing, molding and existing of cracks [4-6].

Today, the use of additives is increasing, scientists are constantly looking for materials that can be used as an alternative to traditional materials, or that have features that enable them to be used for new designs and innovations. In the early ages, hydration of concrete was characterized by a significant thermal release due to the exothermic nature of the water reactions [7-9]. This release of heat causes material deformations and may cause fine and micro-cracks in general concrete structures. This cracking in concrete structures can lead to loss of durability. To predict these thermo-influence deformations and prevent cracking, it is important to clearly define the evolution of the thermal behavior of the interactive component of concrete, namely cement paste [10-12].

Fly ash, silica fume, and metakaolin are prominently applied as cement and concrete additives worldwide to make concrete more durable due to its fine particles, large area of surface, high Silicon
dioxide content and improved concrete properties. Additives have increased in recent years because when mixed with certain proportions, they increase the characteristics of both fresh and hardened concrete like permeability, strength, and durability. While adding fine pozzolanic particles to the mixture, the heat of hydration leading to the formation of pozzolanic and calcium hydroxide is observed. High heats of hydration from silica fume and metakaolin, which reduces setting times. However, fine particle size with high reactivity cause problems to the workability of concrete. Silica fume is very expensive and will accelerate the hydration of cement and compensate for early strength loss and slow reaction rates associated with fly ash to improve performance at an early age and beyond. Metakaolin is expensive and used with cement alternatively and will accelerate the hydration reaction to increase strength both in early and subsequent age and performance of mortar and concrete [13, 14].

It has been reported that the use of MK as an additional cement material enhances the concrete intensity, particularly in the first periods of hydration. It is concluded that the increase in compressive strength of MK concrete is due to the filling effect as MK particles fill the gap between cement particles, accelerating cement hydration and pozzolan reaction in MK. The Pozzolanic reaction is a reaction within silicates and aluminates of the dissolution of MK and CH produced by hydration of the cement, resulting in further CSH and this consequence is comparable to the influence of silica fume. Even though the size of the pores slightly increased in pastes comprising MK, the pore structure of the paste was revised. High pozzolanic activity of pozzolanic materials, like SF and MK, interact with CH emitted in the ordinary Portland cement hydration, which increases the heat of hydration temperature due to the exothermic impact of the pozzolan reaction associated to 100% OPC [15, 16].

2. Literature Review

Langan B W et al. (2002) [1] silica fume and fly ash were used to examine the hydration of the mixtures. It was found that high levels of w/cm fly ash retard more cement hydration than silica fume, but at low w/cm levels, silica fume delays hydration. Papadakis V G (2000) [3] examines the impact of fly ash and silica fume on the durability of PC. It has been found that when additives are used as an aggregate replacement, the depth of carbonation decreases and when additives are used instead of cement, the depth of carbonates increases. Bai J and Wild S (2002) [4] investigation and present as cement replacement metakaolin and fly ash reached a 15% and 40% cement exchange level. It was found that there was an increase in a temperature increase of MK and a decrease in a temperature increase in FA. MK produces the largest delay in the time required to reach the highest temperature when the FA is lower. Kadri E H and Duval R (2002) [5] investigated the effect of fine materials such as (silica fume, quartz dust, and calcite) on accelerated heat of hydration and increased compression strength with 90% Portland cement and with 10% admixture having 0.45 w/c ratio. Kadri E H and Duval (2009) [6] evaluate the concrete heat of hydration having the impact of 10% to 30% silica fume as an alternative to cement with 0.25 to 0.45 w/c percentages. Compared to reference concrete, 10% of silica fume increased the hydration rate and increased the strength of the concrete. Park C K et al. (2005) [10] SF, FA and blast furnace slag is applied to improve the durability, fluidity, and intensity of cement materials. The results showed that BFS is better than FA. Bai J et al. (2000) [11] present durability study with water transport properties, carbonization, chloride penetration and concrete strength (7, 28 and 90 days) with the impact of metakaolin and fly ash in concrete with (w/b ratios 0.4, 0.5 and 0.6), they found that the effect of each additives materials where different form the combined materials additives effect. Low partial cement alternatives and high MK/PFA early strengths have improved, but low MK/PFA rates and higher cement alternatives provide greater strength for 90 days. Brooks J et al. (2000) [14] investigate the high strength concrete setting times through the impact of (fly ash, methacholine, granular slag furnaces, and silica fume). It has been found that additives retarded setting times for high strength concrete, but for MK this was only observed for the replacement level reaches only 10%. Amudhavalli N K and Jeena M (2012) [16] experimental study on the strength and durability properties of silica fume (0, 5, 10, 15 and 20%) is presented as a partial alternative to cement. Improvement in concrete strength and durability was observed with the implication of silica fume. Rafat Seddik (2003) [19] found a notable development in the durability characteristics of concrete by substituting fly ash (10, 20, 30, 40, and 50) with fine aggregate (sand).
concrete. Liu J et al. (2014) [20] examine the hydration rate and cement strength with the effect of fly ash and silica fumes. The higher the rate of fly ash, the higher the peak of the rate of hydration heat evolution and the lower the mechanical strength, and for the higher the silica fume, the mechanical strength increased and the heat of hydration peak evolution. Zhang et al. (2014) [21] consider the influence of (silica fume, slag, fly ash, and zeolite powder) as mineral admixtures on cement paste properties. The invistigation revealed that the best ratio of fine materials is as follows (silica fume=8%, zeolite powder=10%, fly ash=20%, and slag=20%) with the best mixture of two components of 2% slag and 8% silica fume. Terrence R et al. (2000) [22] study the effect of metakaolin with the percentage of 0–20% as cement a partial replacement to control the expansion. Metakaolin of 20% ratio reduces the pore solutions (pH and alkalinity). Ajay B and Vinay D (2017) [23] silica fume with ratios of (0, 5, 7.5, 12.5, 15, 20 and 25%) by the weight of cement used as cement replacement with (w/b=0.42) were investigated to study the different concrete properties at curing age of 7, 14, and 28 days.

Although, many researches existed on the impact of different materials additives, but there is no research conducted a comparison for the efficiency of different additives (fly ash, silica fume, and metakaolin) to the concrete mixture with (0, 5, 10, 15, 20, 25, 30%) percentage of cement weight, and different parameters including impact of additives on (alkalinity, heat of hydration, initial setting time, final setting time, compressive strength and impact of w/c ratio on heat of hydration with three w/c ratio of (0.3, 0.35 and 0.4)).

3. Materials

3.1. Ordinary Portland cement

OPC was utilize in all research studies from the Northern Cement Factory (ASTM Type I) of Iraq. Test results point out that the choose cement conformed to satisfy the requirements of the [Iraqi designation No.5/1984] and conformed to the [ASTM C150-89] identification.

3.2. Fine and Coarse Aggregate

Fine natural sand and gradual natural aggregate size (8mm) were used to ensure acceptable workability. Figure 1 and Table 1 shows the sieve analysis test results and grading curve of sand and coarse aggregate, applied throughout this study related to the prerequisite of the [B.S.882/1992 and No.45/1984 of Iraqi specification].

Table 1. Grading of fine and coarse aggregate.

| Size (mm) | % Limits | Sand Cumulative | Sieve (mm) | (% Passing) | (limits) |
|-----------|----------|-----------------|------------|-------------|---------|
| 4.75      | 100 (95-100) | 14 mm | 100 (100) |
| 2.36      | 100(95-100) | 10 mm | 94 (85-100) |
| 1.18      | 97 (90-100) | 5 mm | 18 (0-25) |
| 0.60      | 93 (80-100) | 2.36 mm | 3 (0-5) |
| 0.30      | 12 (15-50) | | |
| 0.15      | 8 (0-15) | | |

Figure 1. show the grading curve of sand and coarse aggregate.

3.3. Silica Fume (SF)
Intensive gray silica fume was used as a mineral material for research mixtures. The percentages used (0, 5, 10, 15, 20, 25, 30%) by weigh cement (as an replacement to cement). The chemical constitution of the silica fume used in this research complies with the physical and chemical requirements of [C1240-04-ASTM]. Dense silica is a mineral mixture that contains a silicon dioxide of high amorphous content and is a crushed solid pozzolanic substance consisting of very fine spherical particles. It reacts with calcium hydroxide and produces a hydrate of calcium silicate (secondary gel). Silica fume is a remarkably active pozzolanic substance and is an after-effect of silicon or silicon metal production. It is collected from the flue gases coming out of the electric arc furnaces. Silica fume is a very fine powder with particles smaller than 100 times the size of the cement grain. These additives increase the durability, mechanical properties, and workability of concrete. Silica fume consumes calcium hydroxide and also reacts with alkali in concrete. This results in lower alkalinity in the pore solution and less calcium hydroxide in the matrix. This means there are more calcium silicate hydrate and less calcium hydroxide. The pH in the pore water is also reduced. Carbonization can reduce the alkalinity and protection of steel [17, 18].

3.4. Fly ash
FA is generated when 1600 C° of heat subjected to coal and burn. This combustion also generated some incombustible materials merge to form spherical glass drops of iron oxide, alumina, silica, and other by-products. According to [ASTM C 618-05], there are two categories of Fly ash based on the type and origin of coal-generated. Class F is produced by burning anthracites that are mainly siliceous and have pozzolanic properties. Class C, which contains lime and more magnesium oxide content and is produced by burning coal and lignite. Class C fly ash is lighter compared to other materials and at high temperatures, the strength behavior is not evident.

3.5. Metakaolin
At a temperature between 600 and 850 C°, kaolin is converted to MK. MK is a highly reactive pozzolan, but its chemical and physical properties strongly rely on the raw materials adopted, the temperature in process of calcination and finishing; Thus MK was produced with a very diffuse structure with natural cooling. The calcination temperature and duration rely on the mineral composition of the raw kaolin. MK is a complementary cement material compatible with pozzolan N class [ASTM C 618] and the pozzolanic substance has no direct cement value, but with calcium hydroxide chemically reacts to form compounds with cement properties. The substance is a fine white clay mineral conventionally adopted in the creation of porcelain. When MK interacts with Ca(OH)2, it is a silica-alumina founded composite that generates calcium silicate hydrate gel (CSH) and different hydrate compounds at ambient temperature. Figure 2 shows the silica fume, metakaolin and fly ash powder adopted in this research.

![Silica fume, Metakaolin, Fly ash](image)

Figure 2. Additives used in research work.

4. Mixture Proportioning and Experimental Program
Figure 3 shows a flow chart of the research methodology. Table 2 shows all proportional materials and mix design for concrete produced with the effect of the cement weight contribution rate (0, 5, 10, 15, 20, 25, 30%). A study is presented for different measurements such as (impact of additives on alkalinity, impact of additives on the heat of hydration with a fixed w/c ratio of 0.35, impact of additives on initial setting time, impact of additives on final setting and impact of the w/c ratio on heat
of hydration with three w/c ratios of (0.3, 0.35 and 0.4) and the impact of additives on compressive strength. The ratio of the water cementations materials remained constant at (0.35). Dry concrete components are mixed in a mechanical mixer. The heat of hydration temperature was evaluated with an adiabatic situation or isothermal. The hydration evaluation of heat in the present investigation was held out within isothermal situation (25±0.1°C). Thermocouples are used to measure the heat of hydration of concrete, to set the time between 0 and 24 hours and to measure with a thermoelectric device. For compressive strength, 100*100*100 mm\(^3\) concrete cubes have been used and tested for 28 days, using different mixing ratios resulting from different ratios of cement additives, with a view to perform the compressive strength test and tested in accordance with [ASTM C192/192 M-02], using 2000 kN using a capacity testing machine. In the first part of the investigations, a constant initial temperature of 25°C concretemixture was applied. All measurements were made to stabilize the temperature in the concrete under test. Figure 4 presents the alkalinity and heat of hydration measurement used in research work.

### Research Program

- **Mix design**
  - Cement = 544 kg/m\(^3\)
  - Sand = 677 kg/m\(^3\)
  - Aggregate = 1000 kg/m\(^3\)
  - w/c = 0.35

- **Effect of (fly ash, silica fume, and metakaolin) (0, 5, 10, 15, 20, 25, 30%) of cement weight**

- **Effect w/c ratio on heat of hydration**
  - w/c = 0.3
  - w/c = 0.35
  - w/c = 0.4

**Figure 3.** Flowchart of research methodology.

**Table 2.** Material proportioning and test results.

| Mix   | Cement kg/m\(^3\) | Sand kg/m\(^3\) | Aggregate kg/m\(^3\) | w/c | by weight of cement | Peak heat C\(^o\) (%) | Compressive strength (MPa) (%) | Initial setting time (min) (%) | Final setting time (min) (%) |
|-------|--------------------|----------------|-----------------------|-----|---------------------|------------------------|-------------------------------|-----------------------------|-----------------------------|
| Mix M1 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 0     | 58                    | 0.00                         | 60.0                        | 0.00                        | 69                          | 0.00                        | 90                          | 0.00                        |
| Mix M2 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 5     | 56.8                  | -2.07                        | 64.0                        | 10.34                        | 75                          | 29.31                       | 96                          | 65.52                       |
| Mix M3 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 10    | 55.4                  | -4.48                        | 67.0                        | 15.52                        | 83                          | 43.10                       | 100                         | 72.41                       |
| Mix M4 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 15    | 53.8                  | -7.24                        | 69.0                        | 18.97                        | 88                          | 51.72                       | 105                         | 81.03                       |
| Mix M5 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 20    | 52                    | -10.34                       | 70.0                        | 20.69                        | 90                          | 55.17                       | 110                         | 89.66                       |
| Mix M6 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 25    | 50.7                  | -12.59                       | 71.9                        | 23.97                        | 95                          | 63.79                       | 115                         | 98.28                       |
| Mix M7 | 544                | 677            | 1000                  | 0.35| (Metakaolin) 30    | 49                    | -15.52                       | 73.0                        | 25.86                        | 100                         | 72.41                       | 118                         | 103.45                      |
| Mix F1 | 544                | 677            | 1000                  | 0.35| (Fly ash) 0       | 58                    | 0.00                         | 60.0                        | 0.00                         | 69                          | 0.00                        | 90                          | 0.00                        |
| Mix F2 | 544                | 677            | 1000                  | 0.35| (Fly ash) 5       | 55.2                  | -4.83                        | 65.3                        | 12.59                        | 80                          | 37.93                       | 97                          | 67.24                       |
| Mix F3 | 544                | 677            | 1000                  | 0.35| (Fly ash) 10      | 53.9                  | -7.07                        | 68.3                        | 17.76                        | 89                          | 53.45                       | 105                         | 81.03                       |
| Mix F4 | 544                | 677            | 1000                  | 0.35| (Fly ash) 15      | 52.3                  | -9.83                        | 70.4                        | 21.38                        | 94                          | 62.07                       | 115                         | 98.28                       |
| Mix F5 | 544                | 677            | 1000                  | 0.35| (Fly ash) 20      | 50.6                  | -12.76                       | 71.4                        | 23.10                        | 95                          | 63.79                       | 120                         | 106.90                      |
| Mix F6 | 544                | 677            | 1000                  | 0.35| (Fly ash) 25      | 49.3                  | -15.00                       | 73.3                        | 26.38                        | 100                         | 72.41                       | 126                         | 117.24                      |
| Mix F7 | 544                | 677            | 1000                  | 0.35| (Fly ash) 30      | 47.7                  | -17.76                       | 74.5                        | 28.45                        | 107                         | 84.48                       | 128                         | 120.69                      |
| Mix SF1 | 544            | 677            | 1000                  | 0.35| (silica fume) 0  | 58                    | 0.00                         | 60.0                        | 0.00                         | 69                          | 0.00                        | 90                          | 0.00                        |
| Mix SF2 | 544            | 677            | 1000                  | 0.35| (silica fume) 5  | 52.5                  | -9.48                        | 65.9                        | 13.62                        | 80                          | 37.93                       | 100                         | 72.41                       |
Mix SF3 544 677 1000 0.35 (silica fume) 10 51.2 -11.72 69.0 18.97 94 62.07 112 93.10
Mix SF4 544 677 1000 0.35 (silica fume) 15 49.7 -14.31 71.1 22.59 100 72.41 124 113.79
Mix SF5 544 677 1000 0.35 (silica fume) 20 48.1 -17.07 72.1 24.31 105 81.03 135 132.76
Mix SF6 544 677 1000 0.35 (silica fume) 25 46.9 -19.14 74.1 27.76 114 96.55 140 141.38
Mix SF7 544 677 1000 0.35 (silica fume) 30 45.3 -21.90 75.2 29.66 121 108.6 143 146.55

5. Discussion of the Results

5.1. Effect of Additives on Compressive Strength
Three main factors affect the contribution of additives to strength when adding admixtures to concrete. This is the filling effect (pozzolanic reaction, finer particle size leads to more dependable packing and filling capability, cement acceleration of hydration). The filling effect, resulting in a further efficient paste filling, is instantaneous and the raising of cement hydration has a significant effect during within the first 24 hours, and the reaction of pozzolanic provides the higher supplement to strength nearly within the age of 7-14 days. The concrete mixtures compressive strength for 28 days is presented in Figure 5. Can be concluded from figure, that the impact of silica fume gives higher results compared to other additives, then fly ash and finally Metakaolin.

The compressive strengths of the specimens with 30% silica fume, metakaolin and fly ash are highest and silica fume is highest compared with two other specimens. The increasing percentage for silica fume were (0, 13.62, 18.97, 22.59, 24.31, 27.76, 29.66%), and (0, 12.59, 17.76, 21.38, 23.10, 26.38, 28.45%) for fly ash and finally (0, 10.34, 15.52, 18.97, 20.69, 23.97, 25.86%) for Metakaolin.

This may be rely to the increase in the range of the pozzolanic reaction when the additive content of the cement minerals increases up to 30%. For efficient construction application, the capability of the decline in heat formation should be properly evaluated based on even strength relative to equal w/cm. In this context, the addition of additives will reduce heat production on the one hand and remarkably develop the strength of the concrete on the other. The increase in strength due to silica fumes will be attributed to the high fineness leading to increased density, improved filler and pozzolan reaction. Fly ash as a component of binary cement has reduced the compressive strength of the cement with increased content, which will be due to its late reaction, so that until enough high alkalinity of pore water presented, for the reaction of its pozzolanic.
5.2. Effect of Additives on Setting Time

Table 2 shows that additives, as a binary cement component, improved the concrete setting times (initial and final) with higher amount, (due to the fact that Ca(OH)2 does not start until the release of pore water) and improved the cement pastes final setting times related to sufficient Ca(OH)2 is available to ensure higher reactivity. This may be due to a contraction in the Portland cement compound (dilution effect) resulting in pore water with low alkalinity and the following retard in the additives reactivity. Initial and final setting time of the concrete mixtures shown in Figure 6 and 7. Figures yielded that the effect of silica fume were gives the higher results compared to other additives, then come fly ash and finally the Metakaolin. The initial and final setting time of the specimens with 30% silica fume, fly ash and Metakaolin are highest and silica fume is highest compared with two other specimens. The increasing percentage for silica fume were (0, 37.93, 62.07, 72.41, 81.03, 96.55, 108.62%) for initial setting time and (0, 72.41, 93.10, 113.79, 132.76, 141.38, 146.55%) for final setting time, and for fly ash the initial setting time (0, 37.93, 53.45, 62.07, 63.79, 72.41, 84.48%) and (0, 67.24, 81.03, 98.28, 106.90, 117.24, 120.69%) for final setting time and finally (0, 29.31, 43.10, 51.72, 55.17, 63.79, 72.41%) for initial setting time and (0, 65.52, 72.41, 81.03, 89.66, 98.28, 103.45%) for final setting time for Metakaolin.

5.3. Effect of Additives on Heat of Hydration

The thermocouple is a remarkably adaptable device; it is constructed from a couple of pieces of unique wire, combined collectively. One thermocouple was used for each test, as shown in Figure 8, and placed at the mid of concrete specimens to reach the center of the mold to read the variation of temperatures. Additives can greatly decrease the degree and quantity of heat evolution and heat development. Silica fume, metakaolin and fly ash have been used with different percentages. Figure 9 show the result of heat of hydration with different additives. These additives are used instead of cement (cement replacement). All additives can be classified as filler and have different reaction properties, which will lead to different thermal properties. Additives will react as fillers which will consequence in compact microstructure and also will generate a perfect binder. Closed cell structure is deformed due to the
compact composition of the microstructure. Additives will reduce the heat produced while the hydration process continues. A large amount of additives reduces the use of cement, leading to heat reduction. The result shows that the high rate of additives lowers the hydration temperature. The Additives also reduce the pores amount and size. Additives as filler prevent bubbles from joining together and provide uniform pore distribution. The heat of hydration obtained from samples containing 30% silica fume, fly ash and metakaolin is the lowest, and silica fume is the lowest compared to the other two samples. The decreasing percentage for silica fume were (0, 9.48, 11.72, 14.31, 17.07, 19.14, 21.90%), and (0, 4.83, 7.07, 9.83, 12.76, 15.00, 17.76%) for fly ash and finally (0, 2.07, 4.48, 7.24, 10.34, 12.59, 15.52%) for Metakaolin.

Figure 8. Thermocouple and device used in test.

Figure 9. Heat of hydration for different additives percentages.

From figures (10, 11 and 12), the temperature rising curve for all additives were divided into three parts:

1) for all additives curves, there is no increase in temperature from 0 to about 8 hours.
2) After 8 hours there will be an increase in temperature reach to the ultimate temperature in about 14 hours directly to the formation of a large amount of hydration generation.
3) In the third section after 14 hours, the temperature starts to decrease due to the concrete setting in which the reaction rate is extremely steady and the reaction is propagation controlled.
4) The outcomes display that for the same concentration, silica fume is a better heat reduction than fly ash and Metakaolin.

Figure 10. Heat of hydration with

Figure 11. Heat of hydration with
time for Metakaolin.  time for fly ash.

![Figure 12. Heat of hydration with time for silica fume.](image-url)

- **Metakaolin**
  The total heat of hydration of Metakaolin normally not entirely reduces the maximum heat production rate though additionally delays the peak of hydration and the curve is shifted to the left as shown in figure 10. As the Metakaolin ratio increases, the peak becomes wider and the heat generation is faster in the (0% additives). Metakaolin, as a binary cement component, reduced the total heat produced and the maximum rate of heat evolution and increased the period taken to reach the maximum rate with increasing content. The peak heat of hydration for all percentages (0, 5, 10, 15, 20, 25, and 30%) is about [58.0 °C at 11.6 hour for 0%], [56.8 °C at 11.8 hour for 5%], [55.4 °C at 12.1 hour for 10%], [53.8 °C at 12.3 hour for 15%], [52.0 °C at 12.5 hour for 20%], [50.7 °C at 12.7 hour for 25%] and [49.0 °C at 12.9 hour for 30%].

- **Fly ash**
  The entire fly ash heat of hydration commonly relies on the content of CaO. Fly ash not totally reduces the maximum heat production flow however additionally delays the hydration peak as shown in figure 11. While the fly ash proportion develops, the peak grows wider and the heat generation is faster in the (0% additives). Fly ash, as a binary cement component, reduced the total heat produced and the maximum rate of heat evolution and increased the period demanded to extend the maximum rate with increasing content. The ultimate heat of hydration for all percentage (0, 5, 10, 15, 20, 25, and 30%) is about [58.0 °C at 11.6 hour for 0%], [55.2 °C at 12.5 hour for 5%], [53.9 °C at 12.8 hour for 10%], [52.3 °C at 13.1 hour for 15%], [50.6 °C at 13.3 hour for 20%], [49.3 °C at 13.2 hour for 25%] and [47.7 °C at 13.5 hour for 30%].

- **Silica Fume**
  The silica fume total heat of hydration normally not barely reduces the maximum heat production rate, however additionally delays the peak of hydration as shown in figure 12. As the silica fume ratio increases, the peak becomes wider and heat propagation is faster in the (0% additives). Silica fume, as a binary cement component, reduced the total heat generated and the maximum rate of heat evolution and increased the period needed to extend the maximum rate with increasing content. The ultimate heat of hydration for all percentage (0, 5, 10, 15, 20, 25, and 30%) is about [58.0 °C at 11.6 hour for 0%], [52.5 °C at 12.8 hour for 5%], [51.2 °C at 12.8 hour for 10%], [49.7 °C at 13.1 hour for 15%], [48.1 °C at 13.3 hour for 20%], [46.9 °C at 13.2 hour for 25%] and [45.3 °C at 13.5 hour for 30%].
Figure 13. Heat of hydration with time for different additives with 5%.

Figure 14. Heat of hydration with time for different additives with 10%.

Figure 15. Heat of hydration with time for different additives with 15%.

Figure 16. Heat of hydration with time for different additives with 20%.

Figure 17. Heat of hydration with time for different additives with 25%.

Figure 18. Heat of hydration with time for different additives with 30%.

Figure from 13 to 18 and table 4 show that for the same concentration, silica fume is a better heat reduction than fly ash and Metakaolin.

Table 4. Effect of additives on peak heat of hydration with different additives percentage.

| Percentage (%) | Metakaoline |  | Fly ash |  | Silica fume |  |
|----------------|-------------|---|---------|---|-------------|---|
| Time (h)       | Temperature | C⁰ | Time (h) | Temperature | C⁰ | Time (h) | Temperature | C⁰ |
| 0              | 11.6        | 58.0 | 11.6     | 58.0       | 11.6 | 58.0     |           |    |
| 5              | 11.8        | 56.8 | 12.5     | 55.2       | 12.8 | 52.5     |           |    |
| 10             | 12.1        | 55.4 | 12.8     | 53.9       | 12.8 | 51.2     |           |    |
| 15             | 12.3        | 53.8 | 13.1     | 52.3       | 13.1 | 49.7     |           |    |
| 20             | 12.5        | 52.0 | 13.3     | 50.6       | 13.3 | 48.1     |           |    |
| 25             | 12.7        | 50.7 | 13.2     | 49.3       | 13.2 | 46.9     |           |    |
| 30             | 12.9        | 49.0 | 13.5     | 47.7       | 13.5 | 45.3     |           |    |

5.4. Effect of w/c Ratio on Heat of Hydration
Figures from 19 to 22 and Table 5 show the result of the w/c ratio on the heat of hydration for different additives with a percentage of 20% with time. Results in these figures show the more the w/c ratio, the higher the additives are disintegrate and resides in suspension for accelerated decomposition reaction. Thus, additives start to stimulate the response ahead at extra w/c ratios and reduce the period to extend the peak heat of hydration. In the initial few moments of hydration, there is an accelerated relief of alkali ions and Ca2+ of the cement mixtures, the decrease in Ca2+ in the solution enhances the releasing rate and the quantity of heat development, i.e. hydration at this step is rapid by additives. Additives are formed of extremely fine particles which, during combined with water may originate compound and are shortly incorporated with a gel-like layer.

Water may be surrounded in this layer, which should proposed as the foundation of the accelerated water exhaustion of additive compounds. If the w/c ratio is minimal, cement and water appear not develop within complete connection originally as the voids may not be assigned of water. Adsorption reduces the water amount possible for cement hydration following in more limited cement using in the hydration method. Consequently, additives act as a retarder to the method. It can be viewed form figure, that the effect of silica fume was given the lower heat of hydration results compared to other additives, then come fly ash and finally the Metakaolin were firstly at w/c ratio=0.3 the heat of hydration for Metakaolin (49.5 C at 12.8 h), fly ash (48.2 C at 13.6 h) and silica fume (45.8 Co at 13.6 h), secondly at w/c ratio=0.35 the heat of hydration for Metakaolin (52.0 C at 12.5 h), fly ash (50.6 C at 13.3 h) and silica fume (48.1 C at 13.3 h), finally at w/c ratio=0.4 the heat of hydration for Metakaolin (55.4 C at 12.4 h), fly ash (53.9 C at 13.2 h) and silica fume (51.2 C at 13.2 h). In common, the higher the specific surface and the smaller the particle size of mineral admixture enhances the water requirements of concrete.

Table 5. Effect of w/c ratio on peak heat of hydration with different additives percentage.

| w/c  | Metakaolin | Fly ash | Silica fume |
|------|------------|---------|-------------|
|      | Time (h)  | Temperature C° | Time (h)  | Temperature C° | Time (h)  | Temperature C° |
| 0.3  | 12.8      | 49.5     | 13.6       | 48.2         | 13.6      | 45.8          |
| 0.35 | 12.5      | 52.0     | 13.3       | 50.6         | 13.3      | 48.1          |
| 0.4  | 12.4      | 55.4     | 13.2       | 53.9         | 13.2      | 51.2          |

Figure 19. Effect of w/c ratio on heat of hydration for 20% Metakaolin with time.

Figure 20. Effect of w/c ratio on heat of hydration for different additives with 20%.
Figure 21. Effect of w/c ratio on heat of hydration for 20% fly ash with time.

5.5. Effect of Additives on Alkalinity

Figure 23 and Table 6 show the effect of additives with different percentages on alkalinity. From graphs, it may be notice that the effect of silica fume was given the higher alkalinity results compared to other additives, then come fly ash and finally the Metakaolin. In normal concrete without any additives, they will have very high pH. During adding additives, these additives will react with the cement and the reaction will differ since additives will dissolve and control the pH and lower it. In this process, other reactions take place like the pozzolanic reactions and binding of alkalis. By the pozzolanic reaction, the C-S-H composed of silica fume with portlandite (the hydration of cement) will help to immobilize alkalis. The pozzolanas react with the Ca(OH)2 from the cement/water reaction and produces more CSH phase. That lower the Ca(OH)2 concentration and concurrently the pH in the pore solution of the concrete. pH is an essential variable in investigating the characteristics of concrete. Both high and low pH both create obstacles in concrete in the form of corrosion and spalling. The high pH of the cement is due to the presence of portlandite (CaOH2) and after adding in the concrete mix the pH of the concrete decreases after setting due to utilization of portlandite in the development of hydration results like CSH, ettringite, and others. This formation of CSH and other hydration products dense the matrix and reduces the permeability of the chloride or reduces the carbonation resulted in reduced corrosion.

Table 6. Effect of additive with different percentage on alkalinity.

| Mix   | Additive (Alkalinity) | Additive (Alkalinity) | Additive (Alkalinity) | Additive (Alkalinity) |
|-------|-----------------------|-----------------------|-----------------------|-----------------------|
| Mix 1 | (silica fume) 0       | 14.08                 | (Fly ash) 0           | 14.08                 |
| Mix 2 | (silica fume) 5       | 14.02                 | (Fly ash) 5           | 13.99                 |
| Mix 3 | (silica fume) 10      | 13.94                 | (Fly ash) 10          | 13.91                 |
| Mix 4 | (silica fume) 15      | 13.76                 | (Fly ash) 15          | 13.73                 |
| Mix 5 | (silica fume) 20      | 13.65                 | (Fly ash) 20          | 13.62                 |
| Mix 6 | (silica fume) 25      | 13.7                  | (Fly ash) 25          | 13.67                 |
| Mix 7 | (silica fume) 30      | 13.86                 | (Fly ash) 30          | 13.83                 |
| Mix 8 | (silica fume) 35      | 13.9                  |                        |                       |
| Mix 9 | (silica fume) 40      | 13.94                 |                        |                       |
| Mix 10| (silica fume) 45      | 13.94                 |                        |                       |
| Mix 11| (silica fume) 50      | 13.92                 |                        |                       |
Figure 23. Effect of alkalinity on heat of hydration for different additives with different percentage.

6. Conclusions

1. Impact of fly ash, silica fume, and metakaolin on concrete with ratio of (0, 5, 10, 15, 20, 25, 30%) of cement weight, including different parameters (impact of additives on alkalinity, impact of additives on heat of hydration with fixed w/c ratio of 0.34, impact of additives on initial setting time, impact of admixtures on final setting and impact of w/c ratio on heat of hydration with three w/c proportion of (0.3, 0.35 as constant and 0.4) and impact of additives on compressive strength).

2. Filler consequence (results in a further packing of efficient paste), the rise of cement hydration (greatest influence during the first 24 h), and the reaction of pozzolanic (increase the strength around within 7 and 14 days) are three primary factors affecting the supplement of additives to concrete strength.

3. Additives are retarded also postpones the peak of heat of hydration of concrete. Additives, as a binary cement component, reduced the total heat generated and the maximum rate of heat development and increased the period needed to reach the maximum rate with increasing content.

4. The compressive strengths with the rate of 30% silica fume, fly ash and Metakaolin are highest and silica fume is highest compared with two other specimens. The increasing percentage up to (29.66, 28.45 and 25.86%) for silica fume, fly ash and Metakaolin respectively.

5. Additives are a binary cement component increased the setting time, the initial and final setting time of the specimens with 30% silica fume, Metakaolin and fly ash are highest and silica fume is highest compared with two other specimens. The increasing percentage for silica fume were up to (108.62 and 146.55%), and for fly (84.48, 120.69%) and Metakaolin (2.41, 103.45%) for initial and final setting time respectively.

6. The high portion of admixture reduces the heat of hydration and the size of pores. The heat of hydration of the specimens with 30% silica fume, fly ash and Metakaolin are lowest and silica fume is highest compared with two other specimens. The decreasing percentage for silica fume were up to (21.90%), and (17.76%) for fly ash and finally (15.52%) for Metakaolin.

7. The curve of rising temperature for all additives revealed there is no increase in temperature from 0 to about 8h after that there will be an increase in temperature reach to the ultimate in about 14h and finally decrease duo to a concrete setting. For the same concentration, silica fume is a better heat reduction than fly ash and Metakaolin.

8. For 30%, the ultimate heat of hydration is about (49.0 °C) which occur at the time of about (12.9h) for Metakaolin, (47.7 °C) which occur at the time of about (13.5h) for fly ash and finally (45.3 °C) which occur at the time of about (13.5h) for silica fume.

9. Additives rased the reaction formerly at higher w/c ratios and reduce the time to reach the peak heat of hydration. silica fume gives the lower heat of hydration results compared to other additives, then come fly ash and finally the Metakaolin. At (w/c=0.3) the heat of hydration was (49.5 °C at 12.8 h), (48.2 °C at 13.6 h) and (45.8 °C at 13.6 h). At (w/c=0.35) the heat of hydration was (52.0 °C at 12.5 h), (50.6 °C at 13.3 h) and (48.1 °C at 13.3 h). Finally, at (w/c=0.4) the heat of
hydration was (55.4°C at 12.4 h), (53.9°C at 13.2 h) and (51.2°C at 13.2 h) for Metakaolin, fly ash and silica fume respectively.

10. The reduction in pH of the concrete mix before casting and molding affects the early hydration and strength but improves the later age concrete properties. Effect of silica fume were gives the higher alkalinity results compared to other additives, then come fly ash and finally the Metakaolin. Additives will react with the cement and control the pH.

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