Iranian Journal of Materials Science & Engineering Vol. 13, No. 4, December 2016

INVESTIGATING THE RELATIONSHIP BETWEEN HEAT OF HYDRATION AND PHYSICO-MECHANICAL PROPERTIES OF CALCIUM SULFATE HEMIHYDRATE IN THE PRESENCE OF ADDITIVES

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Received: January 2016 Accepted: December 2016

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Abstract: *This article addresses the interplay between heat of hydration and physico-mechanical properties of calcium sulfate hemi-hydrate in the presence of retarding additives such as citric and malic acids and sodium citrate. The heat of hydration was measured using a semi-isothermal calorimeter. Results proved that citric and malic acids had superior impact on hydration and mechanical properties. While the concentration of additives was increasing, the maximum heat of hydration was decreasing from 56.15 cal/g.min for blank sample to 33 cal/g.min for high concentrations of citric and malic acids. Consequently, the measured time to this maximum heat of hydration and thus the induction period were increased significantly from 5 to 105 min. Mechanical results indicated that the increase in the amounts of additive led to the reduction of the compressive strength from 16.25 MPa in the blank sample up to 74% for the highest concentration of malic acid.*

Keywords: *Calcium sulfate, Additive, Setting time, Isothermal calorimeter, Compressive strength*

[DOI: 10.22068/ijmse.13.4.61]

1. INTRODUCTION

Calcium sulfate hemi-hydrate ($CaSO_4$•$0.5H_2O$) is one of the crucial kinds of mineral binders. Hemi-hydrate is highly water-soluble [1]. This solubility in water (hydration) is a major property and also a case study about calcium sulfate hemi-hydrate. Although calcium sulfate can often be used as a decorative indoor building material, efforts to improve the outdoor costs are ongoing. Magallanes et al. investigated the development of the compressive strength for gypsum in the presence of certain additives with underwater curing condition [2]. Additives such as citric acid [3], polysaccharides [4,5], silica fume and slag [2,6,7] are used similarly for plaster and cement in order to control the setting time. As a matter of fact, hydration process is comprised of two steps: solution and precipitation of calcium sulfate hemi-hydrate that finally form dehydrate (gypsum) (as mentioned in equation 1)

$$CaSO_4 \bullet 0.5H_2O + 1.5H_2O \leftrightarrow CaSO_4 \bullet 2.0H_2O + Q \qquad (1)$$

Rate of hydration process depends on many of these factors such as particle size of hemi-hydrate, temperature, pH, type, and amount of additives. This characteristic of binder hydrations is of crucial importance and it can affect the mechanical properties of the produced dehydrate. In fast or slow crystallization of gypsum, its microstructure and interlocking form changes and it directly influences the mechanical strength of the product. Moreover, time needed to achieve complete hydration and final setting determines available time for the workability of plaster. Slower hydration provides more time for the workability. A number of experiments have been performed on hydration process particularly to determine an appropriate retarder that provides desired retarding effect as well as an acceptable strength. Badens et al. studied the influence of various carboxylic acids on the rate of hydration by means of adsorption and conductivity measurements. Their results showed a very high retarding effect of carboxylic acids especially malic and citric acids [8]. Furthermore, an investigation has been done into citric acid as a retarder using heat effect of increasing concentration of additive both on the hydration rate and the compressive strength of gypsum [9]. Magallanes et al. have studied hydration of hemihydrate varying temperature, pH and water-to-solid ratio in the presence of citric and malic acids via using isothermal colorimeter curves [10]. In order to evaluate the impact of carboxylic acids on the hydration process, a research on increasing temperature of mixture has been carried out. The result of this investigation and previous studies confirmed higher retarding effect of citric acid and low effect of tartaric acid [11, 12]. Plasters with different particle size distribution and amount of impurities (in different production conditions) affect hydration process. It has been observed that finer plasters have more hydration rate. Moreover, the influence of impurities was revealed by the study of commercial plaster [13-15]. Several researches have utilized various additives to investigate their influences on hydration process and consequently on physical and mechanical properties of produced gypsum. For instance, hydration process is differently affected by additives such as sodium poly acrylate and cellulose ether as retarders of gypsum nucleation [5,16], sodium polyphosphate with small chains by delaying solution of hemihydrate [17], silica fume and blast furnace slag in various ratios [2].

This study focuses on the correlation between heat of hydration and physical and mechanical properties of calcium sulfate hemi-hydrate in the presence of different additives. Due to the gypsum plaster application, there could be a better understanding of the product behavior so that one can choose the optimal kinds and amounts of the additive, based on data such as heat of hydration, setting rate, compressive strength and water adsorption that are investigated here.

2. EXPERIMENTAL

2. 1. Materials

The used calcium sulfate hemi-hydrate was a kind of commercial hemi-hydrate which is named Stucco. It was supplied by Sepid Gatch Gypsum Company, located in Saveh (in the center of Iran). The chemical composition of the used hemi-hydrate plaster (analyzed by wet chemical method) was mainly composed of $CaSO_4 \cdot 0.5\ H_2O$ with 53 wt% of SO_3. The particle size was determined by sieve method. Therefore, the remaining particles on sieve with mesh number of 50 and 170 were 6 and 26 wt. %, respectively. Four different additives including citric acid (CA), malic acid (MA), and sodium citrate (SC) were used and supplied with analytical grade from Merck Company.

The additives were used in different amounts of 0.04, 0.08, 0.12, and 0.16 wt. % incorporated into the used calcium sulfate hemi-hydrate. They were homogenized in a dry condition and then were used for the tests.

2. 2. Test Methods

In order to measure the heat of hydration, a semi-isothermal calorimeter (heat of hydration calorimeter, 62-L007/A; Controls, Italy) was used. Firstly, the heat capacity of calorimeter was determined, according to ASTM C186-05 (2008). The same water-gypsum ratio was used in all tests (0.68 as determined by DIN method for measuring the consistency). Water was poured in a non-reactive container; the mentioned percent by weight of each additive was introduced to the water and dissolved and then hemi-hydrate powder was introduced by distribution method and mixed well. Afterwards, gypsum plaster powder was added to water and mixed. Then the paste immediately was poured into calorimeter container and calorimeter was sealed to prevent exchanging heat. Temperatures were read and recorded every one minute for the first two hours and every 5 min for the rest of experiment by means of calorimeter thermometer. Collected data could be a representation of hydration temperature versus time. By utilizing determined heat capacity of calorimeter and paste mass, the obtained data was converted to heat of hydration versus time per weight of paste sample (Equation 2).

$$Q = \frac{C.\Delta T}{M} \tag{2}$$

where Q is heat per minute per gram, C is heat capacity (calorie per degree of centigrade), ΔT is

[DOI: 10.22068/ijmse.13.4.61]

temperature difference in regard to basic temperature 24°C and M is weight of paste in calorimeter.

Water demand or water-gypsum ratio was determined by DIN method for measuring the consistency. This type of measurement is widely used in Europe and also in Iran to determine the so-called water-gypsum plaster ratio, that is, the amount of gypsum plaster in grams that can be wetted by 100 mL water. The method consists of sprinkling gypsum plaster over the water at a specific rate without mechanical mixing. The water-gypsum ratio (0.68) was kept constant for all samples during the tests.

To measure the setting times, knife method was used in accordance with BS EN 13279-2 (2005) [18]. To determine the compressive strength, prepared pastes were cast into 2×2×2 cm3 cubic moulds. The moulds were kept at nearly 50% relative humidity to prevent drying and to give enough time to the pastes to set and harden at ambient temperature, i.e. 23 °C. After demoulding, the specimens were cured at 23°C and 50% relative humidity until the testing times (7 and 14 days). From each sample, three specimens were used to determine all times of the compressive strength. The average of three measurements was reported as the final result. The compressive strengths were tested using a Uni-axial hydraulic press (Azmoon Test, Iran). To determine the water adsorption, three specimens (the 7-day cured samples) were weighed and tested after 2 hours of water immersion. Distilled water was used throughout all of the tests.

3. RESULTS AND DISCUSSION

3. 1. Setting Time Versus Heat of Hydration

The obtained heat of hydration curves are comprised of three stages; first stage is induction period, i.e. the time that calcium sulfate hemi-hydrate dissolves in water and Ca^{2+} and SO_4^{2-} are separated, distributed in solution and gypsum crystal nuclei formation are started and no clear change in temperature is reported. In the next stage, the reactions are very fast. Dehydrate conversion, nuclei formation and its growth promote the completion of hydration process. Furthermore, an increase in temperature and peak of hydration curve, due to the increase of speed, are also observed. Afterwards, hydration process is so slow that mixture temperature starts to decrease and finally reach to the basic temperature [8,10-12].

3. 1. 1. Malic Acid

Data presented on Fig. 1 showed that adding 0.04 wt. % of malic acid increased the induction period to 38 min and then produced the ascending stage of the curve with a sharp slop. The maximum heat of hydration was delayed for 60

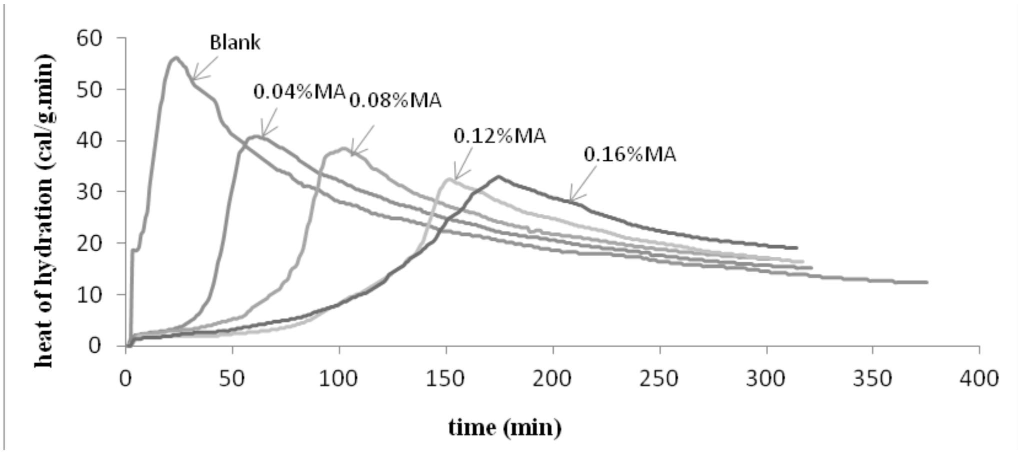

Fig. 1. Heat of hydration versus time for hemi-hydrate with various concentrations by weight of malic acid

[DOI: 10.22068/ijmse.13.4.61]

Table 1. Setting times of hemi-hydrate in the presence of malic acid

	Initial setting (min)	Final setting (min)
Blank hemi-hydrate	5	13
0.04 wt. % malic acid	52	75
0.08 wt. % malic acid	81	138
0.12 wt. % malic acid	110	195
0.16 wt. % malic acid	125	214

min, and its value was 40.90 cal/g.min. Then the mixture gradually reached to ambient temperature (initial temperature) via slowing hydration reaction. It is also observed that initial and final setting time increased to 52 and 75 min for the aforementioned amount of additive, i.e. 0.04 wt. % (table 1).

The increase in malic acid concentration to 0.08, 0.12, and 0.16 wt. % delayed induction period for 70, 80, and 90 min, respectively. The measured maximum heat of hydration for these amounts of additives were 38.32, 32.56, and 38.82 cal/g.min that occurred in 100, 150, and 170 min, respectively.

In spite of lower adjusting structure, due to no blocking effect to adsorption, malic acid is a more efficient retarder in comparison with tartaric acid [8]. Moreover, the relatively low acidity of malic acid, which leads to non-reactivity with impurities, can cause a better retarding effect in all concentration [11]. Heat of hydration and setting time values indicated more retarding effect by increasing concentration of acid.

3. 1. 2. Citric Acid

As shown in Fig. 2, when 0.04 wt. % citric acid was added to hemi-hydrate, induction period increased to 28 min. Maximum of heat release occurred 56 min after mixing and its value was 40.32 cal/g.min which is 15.00 cal/g.min lower in comparison with the blank hemi-hydrate that proves the high retarding effect of citric acid. Among other carboxylic acids, citric acid has a better adjusting structure, because the distance between 2 carboxylic groups of citric acid is exactly equal to the distance between two calcium ions in hemi-hydrate [8].

One small peak before the induction period was observed only in the presence of citric acid and in higher concentration than 0.08 wt. %. In

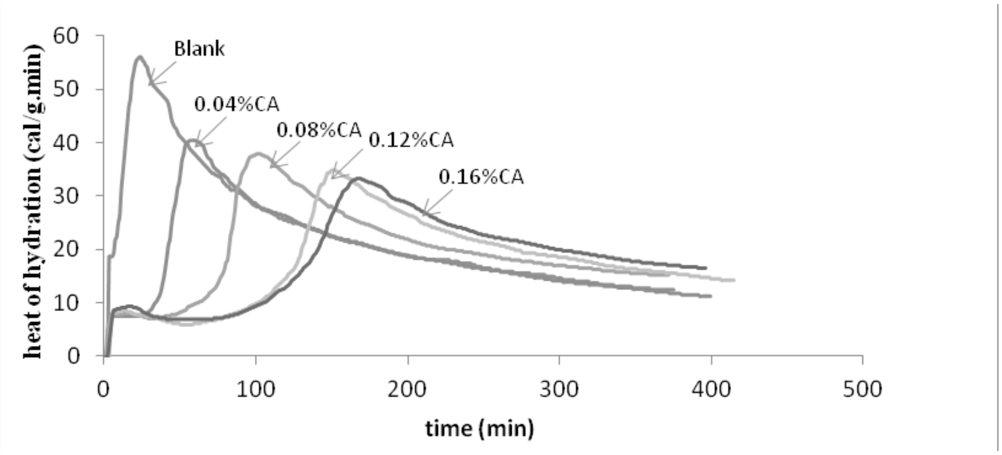

Fig. 2. Heat of hydration versus time for hemi-hydrate with various concentrations by weight of citric acid

Table 2. Setting times of hemi-hydrate in the presence of citric acid

	Initial setting (min)	Final setting (min)
Blank hemi-hydrate	5	13
0.04 wt. % citric acid	41	62
0.08 wt. % citric acid	84	115
0.12 wt. % citric acid	137	172
0.16 wt. % citric acid	141	215

one study, heat of hydration curves have been seen with two peaks that the first peak was attributed to wetting and decomposition of hemi-hydrate particles [10]. Marsches said that small peak in starting hydration occurred due to water adsorption on hemi-hydrate surface [15].

As it's clear in Fig. 2 and has been shown in previous research [11], citric acid retards hydration process until limited concentration and after certain values, this behavior of increasing concentration reduces. However in 0.16 wt. %, induction period and time to maximum of heat released was 105 and 165 min respectively and its heat of hydration was 33.20 cal/g.min. The similar quantities for 0.12 wt% of additives are 100 min and 150 min for the time and 34.83 cal/g.min for heat of hydration. In a previous study it was described that in concentrations more than 1500ppm, retarding effect of citric acid was reduced [9].

Setting time measurements also showed similar results. The intense rise in initial and final setting times in the presence of 0.04, 0.08, and 0.12 wt. % that were 41, 84, 137 min and 62, 115, 172 min respectively, verified the great retarding effect of citric acid. This procedure was slowed down with 0.16% weight of citric acid, as it is shown in Table 2.

3. 1. 3. Sodium Citrate

Influence of sodium citrate as a salt of citric acid, on hydration process has never been studied like carboxylic acids until now. Just organic acid salts of strong bases have been introduced as retarders [12]. In present study, sodium citrate showed relatively minimal impact on hydration process and setting times (Fig. 3). With respect to minimum amount of 0.04 wt. %, heat of hydration reached from 56.15 cal/g.min in blank sample, to 40.38 cal/g.min after 38 min and induction period increased to 8 min. With 0.08 wt. % of sodium citrate, the induction period, maximum heat of hydration and related time to

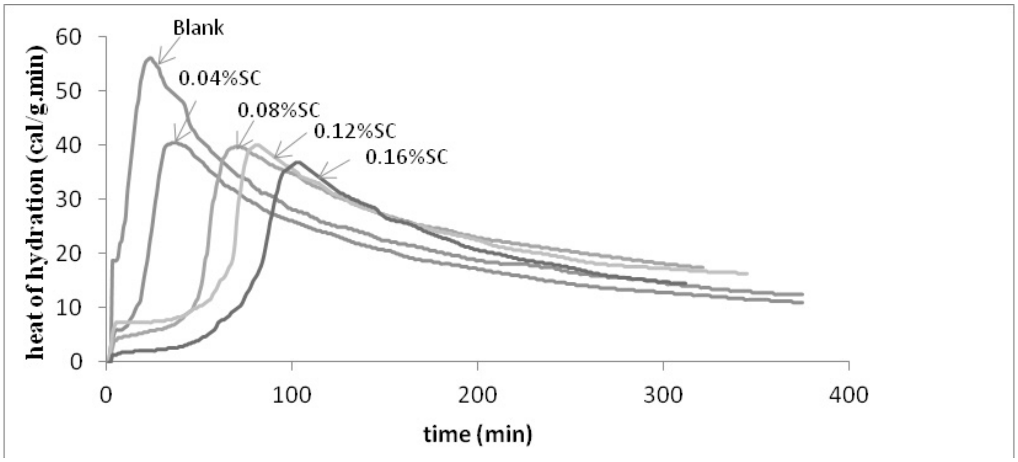

Fig. 3. Heat of hydration versus time for hemi-hydrate with various concentrations by weight of sodium citrate

[DOI: 10.22068/ijmse.13.4.61]

Table 3. Setting times of hemi-hydrate in the presence of sodium citrate

	Initial setting (min)	**Final setting (min)**
Blank hemi-hydrate	5	13
0.04 wt. % sodium citrate	17	31
0.08 wt. % sodium citrate	55	69
0.12 wt. % sodium citrate	63	89
0.16 wt. % sodium citrate	61	87

Table 4. Maximum heat, the time of maximum heat, and induction period for the used additives

	Maximum heat (cal/g.min)	**Time of the maximum (min)**	**Induction period (min)**
Blank sample	56.15	24	5
0.04 wt. % malic acid	40.90	60	38
0.08 wt. % malic acid	38.32	100	70
0.12 wt. % malic acid	32.56	150	80
0.16 wt. % malic acid	32.82	170	90
0.04 wt. % citric acid	40.32	56	28
0.08 wt. % citric acid	37.83	100	60
0.12 wt. % citric acid	34.83	150	100
0.16 wt. % citric acid	33.20	165	105
0.04 wt. % sodium citrate	40.38	35	8
0.08 wt. % sodium citrate	39.73	70	35
0.12 wt. % sodium citrate	40.03	80	40
0.16 wt. % sodium citrate	36.82	100	48

this maximum heat were 35 min, 39.73 cal/g.min and 70 min, respectively. Reduction in retarding effect occurred approximately in 0.16% with citric acid and in concentrations over 0.08 wt. % with sodium citrate because of similar reasons.

The initial and final setting times were measured 17 and 31 min in the presence of 0.04 wt. % of sodium citrate as summarized in table 4. Initial setting time with 0.08, 0.12, and 0.16 wt. % via weight were 55, 63, and 61 min that illustrate the reduction of retarding effect by increasing concentration of sodium citrate like that was described for citric acid.

Table 4 shows the maximum heat, the time of maximum heat, and induction period for the used additives in different concentrations compared to the blank sample.

3. 2. Compressive Strength

Figs. 4 to 7 show the obtained compressive strength in the presence of the used additives after 7 and 14 days curing times. Investigation into the effect of malic acid on hydrated hemi-hydrate compressive strength indicated intense decrease in the strength, even despite the trace amount of acid. As it has been mentioned in slow hydration, with respect to the slow process of completion and hemi-hydrate alteration to dehydrate, the final compressive strength of samples were achieved posterior. Actually, in high concentration of major retarders and

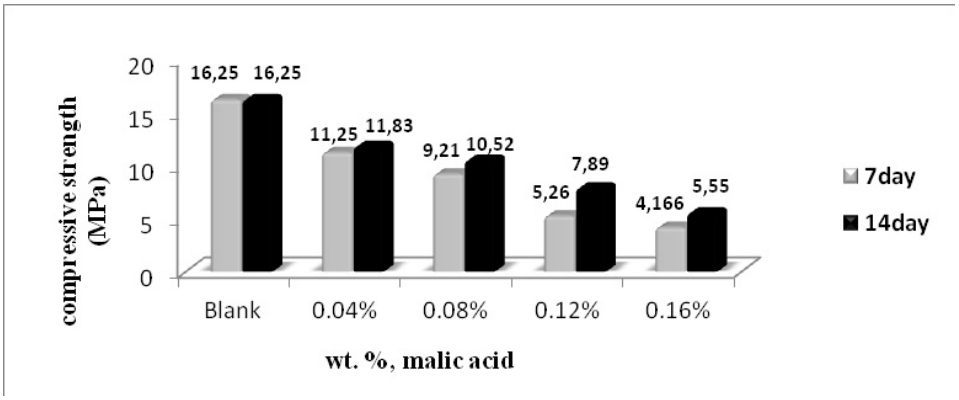

Fig. 5. Compressive strength of hydrated hemi-hydrate with malic acid, after 7 and 14 days of curing time

consequently slow hydration, differences between the 7-day and 14-day compressive strength increased. This result especially could be seen in Fig. 5 with malic acid. The greater rate in hydration process, the higher development in the compressive strength occurred. After the completion of hydration, the compressive strength development would be insignificant [14]. Therefore, the more intense the retarding effect of additives and their concentrations are, the slower hydration and thus the lower the compressive strength is.

Dehydrate crystals have needle shape and interlocking [11] so that the introduction of malic and citric acids cause to larger crystals. In high concentration of additives, macro and micro defect is indicated and this state was observed with tartaric acid. This leads to the decrease of the compressive strength. Moreover, Badens introduced interlocking structure and interactions among crystals as a major factor in development of the compressive strength [8].

Citric acid had less effect on hydration in comparison with malic acid (Fig. 6). By introducing 0.04 wt. % of citric acid, 7-day and 14-day compressive strength reduced from 16.25 MPa in blank hemihydrates to 12.5 MPa. In this concentration, hydration process was not very fast yet and the degree of hydration after 7 days was close to completion. Therefore, 7 days curing time, final compressive strength occurred. Then gradual decrease in citric acid concentration affects the strength because of loss in effect on hydration in high concentrations. Lanzon also observed that citric acid can reduce the compressive strength of dehydrate by reducing

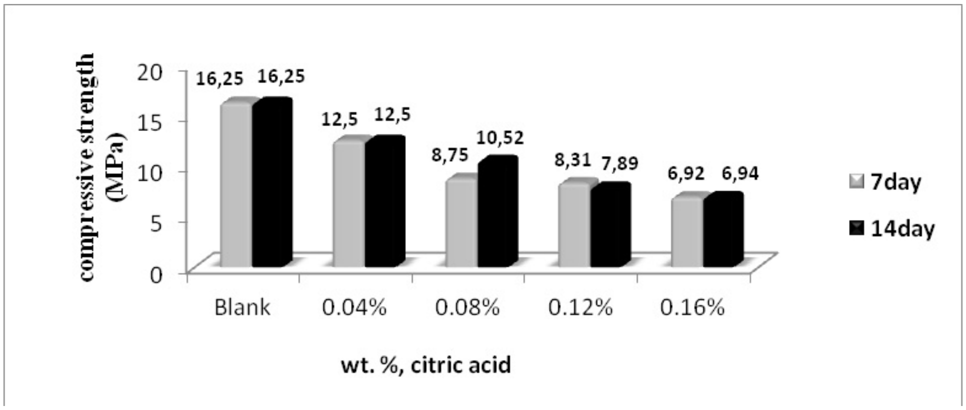

Fig. 6. Compressive strength of hydrated hemi-hydrate with citric acid after 7 and 14 days of curing time

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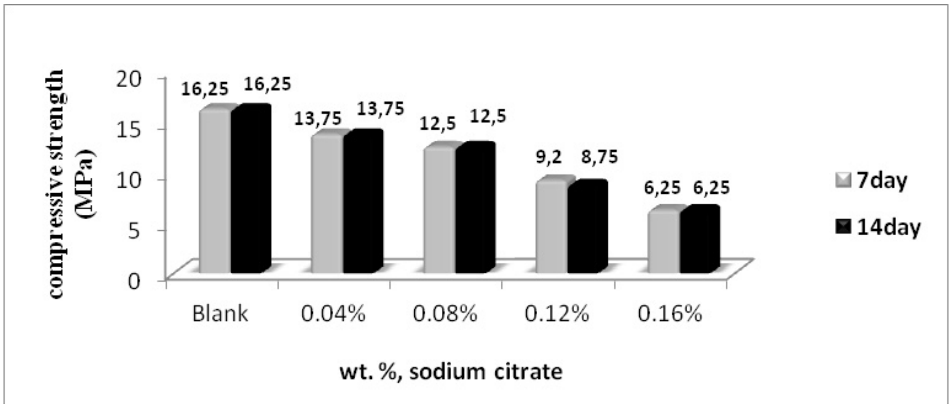

Fig. 7. The compressive strength of hydrated hemi-hydrate with sodium citrate after 7 and 14 days of curing time

the interlocking structure [9].

Influence of sodium citrate on the compressive strength as shown in Fig. 7, was fewer than malic and citric acids. In all concentrations of sodium citrate, the compressive strength development approximately finished in initial 7 days and after this time no more increase in strength was observed. This can be attributed to the hydration completion in a short time.

3. 3. Water Adsorption

2-hour water adsorption for hydrated hemi-hydrate is their physical property measured in the presence of additives. The effect of the used additives on water adsorption and relationship with other properties were investigated, here.

As shown in Table 4, increasing concentration of sodium citrate, didn't influence the water adsorption greatly, but by increase in concentrations of malic and citric acid from 0.04 wt. %, the water adsorption gradually decreased. For instance, in the presence of 0.04, 0.08, 0.12, and 0.16 wt. % of malic acid, 2-h water adsorption measured 28.36, 28.23, 25.56, and 24.08%, respectively. Fig. 8 showed a trend for the relationship between heat of hydration and water adsorption of malic acid in different percentages. As seen, with decrease in the maximum heat of hydration, a decrease was also occurred in the 2-h water adsorption. This behavior is in compatible with the other studied retarding additives, i.e. citric acid and sodium citrate. Also, this could be a similar trend with the results obtained from compressive strength (Fig. 5).

Table 4. 2-h water adsorption with different additives

	Malic acid	**Citric acid**	**Sodium citrate**
Blank sample	27.82	27.82	27.82
0.04 wt. %	28.36	29.14	28.41
0.08 wt. %	28.23	26.98	25.83
0.12 wt. %	25.56	26.41	26.14
0.16 wt. %	24.08	24.64	27.05

[DOI: 10.22068/ijmse.13.4.61]

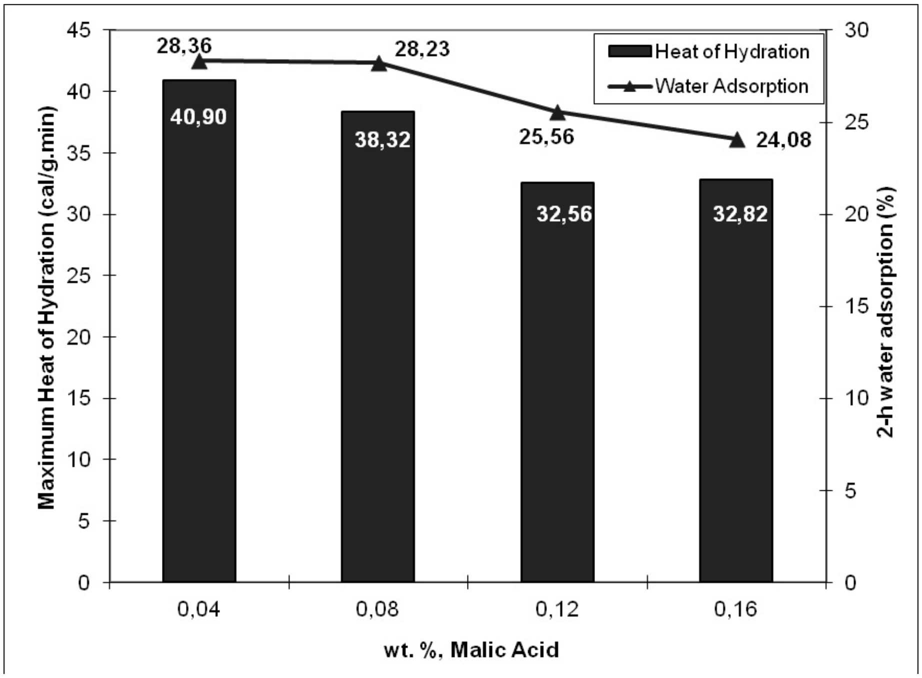

Fig 8. 2-h water adsorption of hydrated hemi-hydrate with malic acid in relation with the maximum heat of hydration

4. CONCLUSIONS

Additives have different effects on hydration process of calcium sulfate hemi-hydrate and also on mechanical properties of produced gypsum. Here, it was tried to find out the influence of several retarders such as malic acid, citric acid and sodium citrate on the hydration process and also on mechanical properties. According to such data, one can find the existing correlation between hydration process and physico-mechanical properties of gypsum which could be very useful when the mix batching is designed in the gypsum wallboard industries. For 0.04 wt. % of malic and citric acids maximum of released heat of hydration, time to maximum heat and induction period were 40.90 cal/g.min, 60 min and 36 min for malic acid and 40.32 cal/g.min, 56 min and 28 min for citric acid, respectively. Citric acid had less effect on hydration in comparison with malic acid so that for 0.04 wt. % of citric acid, 7-day and 14-day compressive strength reduced from 16.25 MPa in blank hemihydrates to 12.5 MPa. More strong retarders decreased water adsorption from 27.82% for blank sample to 24%. Consequently, a retarder can slow down hydration rate and setting times to provide more time to make desired changes in paste and also can reduce the compressive strength at the curing time. Reducing water adsorption can provide a higher compressive strength in a wet curing condition or outdoor building materials.

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