

Treatment of the Local Construction Gypsum Weak Points by the Addition of 4% w/w White Portland Cement

Khalil, Rabah Ali^{*+}; Al-Rasheed, Mohammed Saud

Department of Chemistry, College of Science, University of Mosul, Mosul, IRAQ

ABSTRACT: *The amazing properties of structural gypsum make it as a miracle material for finishing construction processes, especially from the health and the environmental point of view. Chemically, the binding forces between gypsum molecules are limited to dipole-dipole interactions (hydrogen bonding) rather than that of fixed conventional bonds. Such relatively weak bonds are responsible for the two common weak points including the water solubility and the relatively low hardness. Therefore, white Portland cement was suggested as an additive for treating those essential disadvantages of construction gypsum. Samples of different ratios at 0.0%, 0.5%, 1.0%, 2.0%, 3.0%, 4.0%, 5.0%, 6.0% and 8.0% w/w of white cement to gypsum were made using 0.07x0.07x0.07m and 0.05x0.05x0.05m test cubes. The standard tests of physical and mechanical properties including hardness, compressive strength, setting time, and water resistance were measured. The results indicate that the presence of cement as an additive could eliminate the weak points of construction gypsum without any negative side effects. The study was supported by an aging investigation using thermodynamic and kinetic analyses. In conclusion, it was strongly recommended to exploit the white cement as an additive at a ratio of 4% w/w or 4.5% v/v to improve the physical properties of building gypsum. It was found that the presence of white cement at the optimum ratio of 4.0% w/w is not limited to eliminating the weak points of gypsum including the relatively low hardness and water solubility, but it extends in supporting other important properties including both the compressive strength and setting time. The suggested additive has many desirable characteristics such as availability, healthy, economical, odorless, no coloring, used in few ratios, easy to deal with, and no volatile organic compounds (VOCs). The presented success can be applied by the construction industry to produce improved gypsum with no weak points.*

KEYWORDS: *Construction gypsum; Gypsum Plaster; White Portland cement; Construction; Setting time; Hardness.*

INTRODUCTION

The city of Mosul is the capital of the Nineveh Governorate belongs to Iraq (Mesopotamia), where it is famous for its richness in lime minerals. In the past, gypsum was used as a binder for construction rocks as well

as a plaster for finishing both outside and inside walls and roofs. Then, Portland cement has replaced the gypsum for binding purposes due to its high resistivity to water and significantly greater strength and hardness than that of

** To whom correspondence should be addressed.*

+E-mail address: rakhali64@yahoo.com

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gypsum [1]. Currently, the use of gypsum plaster is mainly captured by finishing processes of inside walls and roofs of buildings except for kitchens and bathrooms. In general, from the chemistry point of view, gypsum is considered one of the soft sulfates that occurs naturally and consists of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Indeed, the employment of gypsum plaster for interior construction gives several advantages due to its substantial properties [1-3]. Such properties could make gypsum as a miraculous material, particularly from the health and environmental aspects. There is no doubt in mentioning that the lime materials may be considered as the second womb of non-milk animals (eggshell), which are suitable for the care of the fetus, and at the same time, these materials exist in our body compositions such as bones and teeth. In addition to the economic aspects of gypsum, the relatively good thermal and sound insulation, soothing the inside climate as it absorbs the excess moisture and in drought, it gives moisture, and its ability to absorb toxins from the air such as carbon monoxide gas (purifies the air inside the room) [2,3]. Moreover, gypsum is considered an acidic salt derived from a strong acid (H_2SO_4) and a weak base ($\text{Ca}(\text{OH})_2$) which therefore will be an inadequate medium for harmful microorganisms such as bacteria, germs, fungi, and molds. On the other side, gypsum has two disadvantages that arise from the relatively low resistance towards water and humidity and also from the relatively low hardness as it is smaller than that of human nails. Therefore, serious efforts should be taken into account in order to treat those weak points which may lead to making gypsum as the material of choice for the inside finishing of buildings. However, considerable attention must be taken into account throughout solving this problem by avoiding any negative effects due to the suggested treatment on the original properties of gypsum. Furthermore, the suggested additive materials for accomplishing this task must have the following characteristics: taken in small ratio, cheap, available, healthy, stable, and not disturbing the professionals of gypsum plaster, particularly in decreasing the setting time.

According to the literature, there are several articles concerning the development of gypsum plaster were announced, but there is no specific paper that has the same present objective for treating the weak points of gypsum. Most of these published articles were focused on the effect of various additives on the setting time [4-8], compressive

strength [4,6,8-16], hardness [5,6,9-12], water resistivity [9,12,16-18], and thermal insulation [19,20-23]. Zhang *et al.* [8] published the most related work concerned with the effect of eight retarders including sodium tartrate, melamine, tartaric acid, sucrose, salicylic acid, white cement, citric acid, and sodium triphosphate on the setting time and strength of building gypsum. The other related studies were concerned with other types of additives including clay, sand, wasted polymers, rubber, fibers, and so on. Therefore, one could realize that most of the previously respected works may be located within the term of trial and error rather than depending on the fundamental principle of science. However, the dipole-dipole (commonly called H-bonding) interactions between water molecules that belong to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are responsible for the binding between calcium sulfate molecules. But, at the same time, the strength of the attraction forces of such intermolecular interactions is not relatively strong like those of fixed bonds between atoms such as covalent and ionic bonds. Such weak interactions between gypsum molecules have been practically confirmed by Aquilano *et al.* [24] using X-ray crystallography. They have shown that the structure of gypsum has a monoclinic system and the H-bonding is the whole responsible for the binding between calcium sulfate dihydrate molecules as can be represented by Fig. 1 [24]. In this Fig., one can observe the water molecules of blue color balls are interacting with each other via H-bonding which demonstrates the binding phenomenon between calcium sulfate dihydrate molecules. It should be noted that the binding by H-bond also was found using X-ray crystallography for the formation of polymeric chains by inorganic complexes [25]. Hence, the relatively weak molecular interactions of H-bonding between gypsum molecules are responsible for producing the two weak points of construction gypsum. Therefore, the enhancement of the binding strength between gypsum molecules may be obtained by making the binding not dependent merely on H-bonding. In this work, the employment of Portland white cement as an additive to gypsum plaster was suggested in order to eliminate the practical weaknesses of such an interesting material. Indeed, after the period of setting time, the white cement differs substantially from that of gypsum in both water resistivity and mechanical properties. In general, the white cement is made up of three main components:

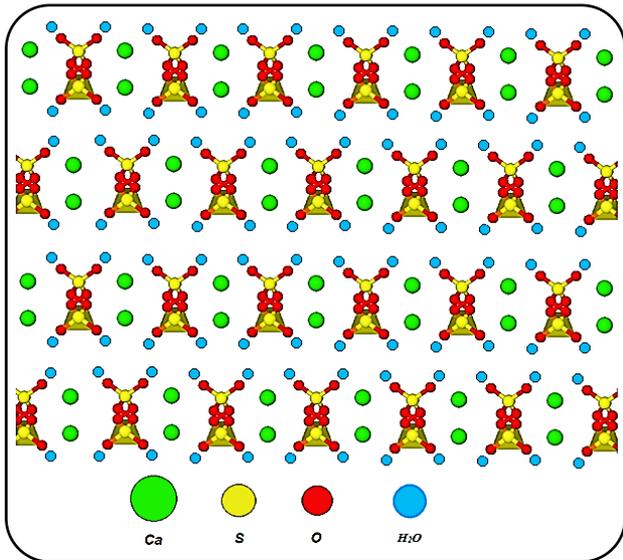


Fig. 1: Illustrates schematically the structure of gypsum as the H-bonding is the whole responsible for the binding between calcium sulfate dihydrate molecules [24].

tricalcium silicate ($3\text{CaO}\cdot\text{SiO}_2$), dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), and tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) [26]. Tricalcium silicate and dicalcium silicate are responsible for adding considerable strength after 2-7 days and one month, respectively. The role of tricalcium aluminate is for instantly setting as well as for the internal strength that fills the space in the lattice [27]. The novelty of this work refers to the treatment of the weak points of construction gypsum using white cement as an additive according to the basics of science. This novelty is also extended to the employment of kinetic and thermodynamic analyses for examining the effect of the presence of the suggested additive on the aging of building gypsum.

EXPERIMENTAL SECTION

Materials

The gypsum plaster used for the finishing processes of the building was brought from local sources with specifications that fall within the Iraqi standards IQS 27-1985 and IQS 28-1988 [28]. The traditional white Portland cement was taken from the market and supplied by a Turkish company (Cimsa Ciminto Sanayi ve Ticaret A.S) according to the English standards EN 197-1:2011.

Procedure of mixing

In order to obtain more reliable results, the mixing procedure was carried out in a similar manner to that of

Table 1: Lists the weights of plaster gypsum and white cement at each ratio.

| Cement to gypsum ratio % (w/w) | Gypsum weight (kg) | Cement weight (kg) $\times 10^3$ |
|--------------------------------|--------------------|----------------------------------|
| 0.0% | 2.400 | 0.0 |
| 0.5% | 2.388 | 12 |
| 1.0% | 2.376 | 24 |
| 2.0% | 2.352 | 48 |
| 3.0% | 2.328 | 72 |
| 4.0% | 2.304 | 96 |
| 5.0% | 2.208 | 120 |
| 6.0% | 2.256 | 144 |
| 8.0% | 2208 | 192 |

local building professionals. The general mixing method was made by weighting 2400g of plaster gypsum and then adding using prose method 1700 mL of tap water in a suitable bowl. The mixture was mixed until getting a liquefied paste then poured into $0.07 \times 0.07 \times 0.07\text{m}$ or $0.05 \times 0.05 \times 0.05\text{m}$ cubic templates depending on the requested test method. The same procedure was also applied when the presence of white cement as an additive at 0.5%, 1.0%, 2.0%, 3.0%, 4.0%, 5.0%, 6.0%, and 8.0% w/w ratios according to the listed weights in Table 1. The dry materials of plaster gypsum and white cement at different ratios were mixed carefully and then sieved in order to enhance the mixing process and poured into an identical amount of water (1700 mL) in a similar manner to that in the absence of the additive.

Testing program

The measurements were made through suitable instruments after leaving the cubic samples for seven days in a non-humid place at room temperature in order to provide a similar environment to that of the construction field. The hardness of cubic samples ($0.07 \times 0.07 \times 0.07\text{m}$) has been measured using Shore D hardness Durometer for the indentation hardness of non-metallic materials which is provided by the Chinese Gullin Digital Electronic Co., Ltd. At least 10 measurements were done for each sample from different faces in order to take the average as well as to check the reproducibility of the observed data. The compressive strength of $0.07 \times 0.07 \times 0.07\text{m}$ samples was estimated using compressive strength instrument model DI-09-CON which

supplied from ALFA Turkish Company with loading rate equal to 0.6 KN/s. The compressive strength in MPa unit was determined using the following relationship.

$$\text{Compressive strength (MPa)} = \frac{\text{Force at point of failure (N)}}{\text{Area of cross section (mm}^2\text{)}} \quad (1)$$

The measurement of setting time was carried out according to the standard procedure using Vicat apparatus (ASTM C472–99) [7, 29]. The used Vicat device consists of a graduated frame ended with a movable plunger ($300 \pm 0.5\text{g}$) of 1.0 cm diameter with a needle diameter of 0.1 cm. The surface roughness of gypsum samples was explored using Motic-MLC-150 digital microscope with a magnifying power of 200x (made in China). The densities for the gypsum and white cement before use were measured using the remodeled density method throughout a fixed standard template for this purpose in a similar manner to that of sand. The Thermal Gravimetric Analysis (TGA) of the powdered samples was made using Shimadzu GA-50 Thermogravimetric Analyzer.

The effect of the presence of water on the solubility of gypsum was measured for cubic samples ($0.05 \times 0.05 \times 0.05\text{m}$) at all ratios of the additive (0.0%–8.0% w/w). In order to estimate the exact weight of the dissolved material, the samples were dried in drying oven at 75°C (not 100°C in order to avoid dehydration and also to give more realistic results) until no change in samples weights were detected. Then the weighted samples were covered using a plastic film in order to avoid the effect of humidity and then cooled and inserted in water at room temperature with timekeeping. Same procedure was carried out after pulling the samples from water at definite time in order to calculate the loss in weight due to the solubility in water. The water or moisture absorption ratio % (w/w) was carried out using the following formula.

$$\text{Water absorption ratio \%} = \frac{\text{Weight of water absorbed (g)}}{\text{Weight of the dry sample (g)}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Fig. 2 exhibits the relationship between the hardness and the ratios of added white cement for $0.07 \times 0.07 \times 0.07\text{m}$ samples after a period of one week for natural curing that enhance the reliability of the results. Interestingly,

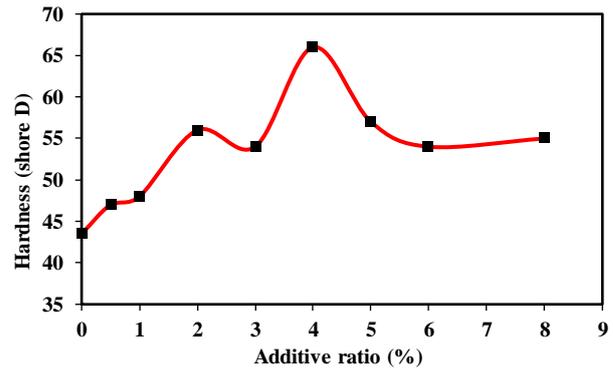


Fig. 2: The relationship between hardness and additive ratio (w/w) of white cement after one week of natural curing.

the results show a remarkable increase in hardness due to the presence of white cement with a maximum at 4% w/w ratio. The reason for this maximum may be related to that at this optimum concentration the additive may only reinforce the binding between gypsum molecules. But, when the concentration of white cement increases there may interact with itself rather than with gypsum molecules which may lead to part of the separation between gypsum and cement molecules. Thus, the hardness increases by a ratio of 52% which definitely makes the hardness of gypsum is more than that of human nail in contrast to that of no additive gypsum.

The effect of the presence of white cement as an additive on the compressive strength was explored. Again, as it was observed with the hardness, the presence of this additive makes a substantial increase in the compressive strength with a maximum at the same ratio of 4% (w/w) as shown clearly in Fig. 3. In other words, at the ratio of 4% the compressive strength enhanced by a ratio of more than 100% due to the presence of white cement. The same trend of the effect of the presence of the suggested additive for both hardness and compressive strength can be attributed to the linear relationship between those properties as it was already found by Kim [30] for methyl methacrylate-based polymer concrete. In general, the reason for the enhancement of the above-mentioned mechanical properties of construction gypsum due to the presence of the additive may be attributed to the additional forces that caused by white cement with gypsum molecules in contrast to that of only hydrogen bonding. On the other hand, the reason of the presence of the maxima in mechanical properties at 4% may be accused to that at this ratio the molecules are arranged in such a way that could give the maximum

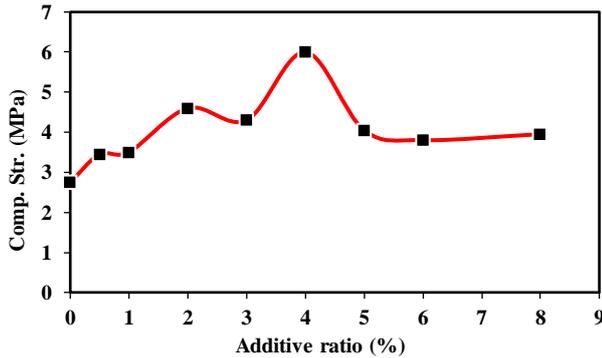


Fig. 3: The relationship between compressive strength and additive ratio (w/w) of white cement after one week of natural curing.

interaction forces which lead to the best packing between the molecules. Hence, it is apparent that the ratio of 4% (w/w) of white cement to gypsum can be considered as the optimum ratio if there is no disadvantages in resistivity towards water and humidity.

It should be noted that the investigation of water resistivity should be done using dry samples in order to estimate the loss in weight in a more accurate way. Table 2 lists the dissolved amounts of samples in water at different ratios of the additive with time. The results importantly show that the presence of the additive leads to substantial resistance towards solubility in water. The results of Table 2 also display that the water resistivity increases with increasing the amount of additive. It is not surprising that the samples in the absence of the additive and even at the low ratio of 0.5% are completely dissolved in the water. The reason for this may be accused to the competitive interactions between the solvent molecules with that hydration molecules of gypsum as both using hydrogen bonding for the binding manner. In other words, the hydrated molecules of gypsum which bind themselves by hydrogen bond leave this bonding in order to make an alternative hydrogen bond with that of water (solvent) molecules, and then make the gypsum quite soluble in water. However, the attractive forces between cement molecules do not depend only on the hydrogen bonding which then makes the concrete as water resistance in comparison with that of gypsum. Therefore, the presence of cement as an additive increases the resistivity of construction gypsum towards water due to the presence of other types of intermolecular attraction forces as not depending only on the hydrogen bonding. In general, the present treatment for the weak points of gypsum due to the presence of white cement can be attributed to the reaction

Table 2: Amount of gypsum dissolved (g) in water with time of 0.05x0.05x0.05m samples after drying by drying oven at 75°C.

| Ratio % | Dissolved weight g (S≡ Dissolved) | | | | |
|---------|-----------------------------------|--------|--------|---------|---------|
| | 1 Days | 5 Days | 8 Days | 15 Days | 22 Days |
| 0.0% | S | S | S | S | S |
| 0.5% | S | S | S | S | S |
| 1.0% | 86.10 | S | S | S | S |
| 2.0% | 46.52 | 16.06 | 15.78 | 9.61 | 7.91 |
| 3.0% | 14.85 | 7.34 | 4.178 | 2.60 | 1.70 |
| 4.0% | 11.90 | 3.46 | 2.25 | 0.58 | 0.40 |
| 5.0% | 9.29 | 4.13 | 3.00 | 2.00 | 0.33 |
| 6.0% | 5.75 | 4.61 | 1.93 | 1.00 | 0.64 |
| 8.0% | 5.13 | 3.48 | 1.20 | 0.76 | 0.11 |

of gypsum with tricalcium aluminate which can be represented by following equation [27].

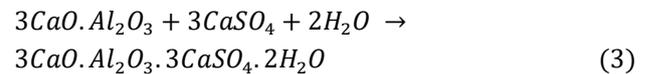


Fig. 4 exhibits the relationship between the solubility of gypsum samples in water against the additive ratios of white cement. The equilibrium constants of solubility in water (K_{ws}) after a period of 22 days (taken from Table 2) were estimated according to the following model, as they listed in Table 3.

$$K_{ws} = \frac{\text{lost weight of the sample (g)}}{\text{Remaining weight of the sample (g)}} \quad (4)$$

The results indicate that the value of K_{ws} decreases with increasing the ratio of the additive. The standard free energy (ΔG°) of the solubility process has been measured using the following equation [31].

$$\Delta G^\circ = -nRT \ln K_{ws} \quad (5)$$

Where n is the number of moles which equal to 1, R is the gas constant and T is the absolute or Kelvin temperature. The results show that the sign of the ΔG° becomes positive due to presence of the additive in a ratio of more than 1% (Table 3). In other words, the solubility of construction gypsum changes from spontaneous to nonspontaneous due to presence of the white cement as an additive. It is clearly that the ratio of 4% (w/w) of the suggested additive can be considered as a sufficient ratio for improving the construction gypsum throughout eliminating its weak points. Hence, according to the above interesting results, one could suggest that the 4% (w/w) ratio of white cement to gypsum is the typical ratio for improving this important building material.

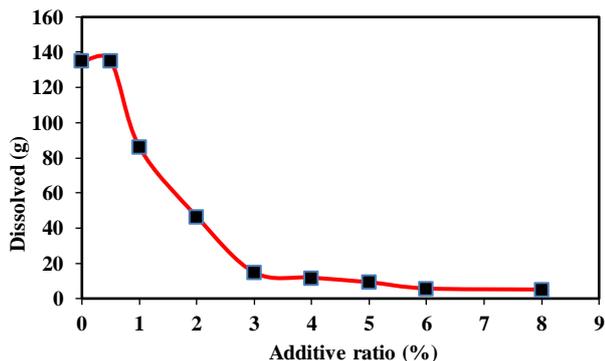


Fig. 4: The relationship between the amounts dissolved in water after one day of submerging the cubic samples into water versus additive ratio (w/w) of white cement.

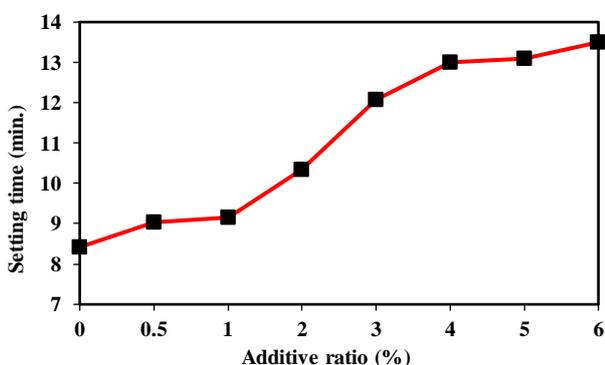


Fig. 5: Effect of addition of white cement at different ratio versus the setting time at room temperature.

In general, it should be borne in mind that the complete success of the present improving process must not be accompanied with any negative side effects for other important advantages of gypsum. Therefore, the effect of the presence of 4% (w/w) white cement to gypsum for other related properties must be investigated in order to confirm the complete success of the present development. Actually, the setting time can be considered as a very important factor in the field of construction, because the relatively short period of setting time will not be enough for finishing processes by professionals and leads to the waste a lot of cured (hard) materials. Therefore, the effect of the presence of white cement as an additive at different ratios on the setting time of gypsum was explored (Fig. 5). Remarkably, Fig. 5 shows there is a remarkable increase in the period of setting time of gypsum with the increase in the ratio of additive. For example, at the selected optimum ratio of 4%, the setting time increased by a ratio of 54.4%. Indeed, the present achievement of improving the property of setting time could give substantial support to the suggested additive

Table 3: Solubility equilibrium constants (K_{ws}) for the solubility of gypsum cubic samples in water after 22 days of immersion and 30°C.

| Ratio % | K_{ws} | ΔG° kJ/mol |
|---------|----------|-------------------------|
| 2.0% | 0.06220 | 6.999 |
| 3.0% | 0.01280 | 10.984 |
| 4.0% | 0.00300 | 14.640 |
| 5.0% | 0.00250 | 15.100 |
| 6.0% | 0.00480 | 13.460 |
| 8.0% | 0.00082 | 17.910 |

in comparison with that of published studies. For example, Al-Ridha et al. [9] studied the possibility of improving the setting time and compressive strength of local gypsum using three additives (silica fume, tree glue powder and polyvinyl acetate). They found that the use of all these additives (altogether) leads to best possible treatment for both properties simultaneously.

Another important characteristic of gypsum, is ability of controlling the climate by absorbing the moisture at high humidity and then released at dry summer weather. Therefore, the effect of the presence of 4% (w/w) of the suggested additive on moisture absorption was examined (Eq. (4)). The results indicate that there is no appreciable effect on this property due to presence of this amount of white cement, as the water absorptivity in the absence and presence of 4% of additive are equal to 40.92% and 39.26%, respectively.

The effect of the presence of the additive at a ratio of 4% on the surface roughness of gypsum also was inspected. Actually, the surface roughness of gypsum plays a good role in absorbing the toxins from the air [2]. The results exhibit (Fig. 6) there is a positive effect towards surface roughness due to presence of the additive at the selected ratio which may also give support to the present claim. The GTA analysis of 0.0% and 4.0% samples showed a comparable thermal gravimetric behavior indicating there is no harmful effect on the thermal stability due to presence of 4.0% white cement as an additive to gypsum.

Generally, it seems quite necessary to investigate the effect of the presence of additive on the aging, particularly when one deal with the effect of additives for improving purposes. Consequently, kinetic study for predicting the effect of the additive on the shelf life must be taken under account [32-34]. Thus, the developed kinetic model for aging purpose can be derived according to the change in



A: In the absence of additive



B: in the presence of 4% (w/w) white cement

Fig. 6: The images of digital microscope with a magnifying power of 200x display the surface roughness of gypsum samples (A) in the absence the additive, (B) in the presence of 4% (w/w) white cement.

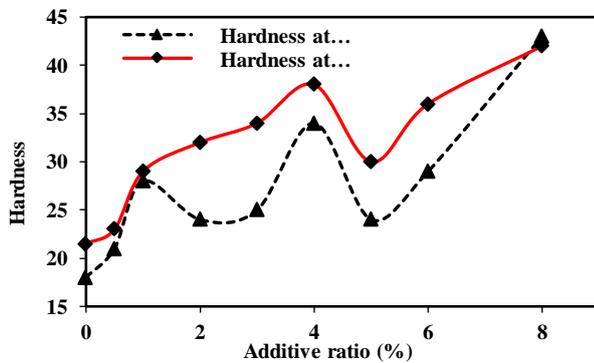


Fig. 7: The effect of aging on the hardness at different ratios of added white cement after 36 days at 60°C and 85°C.

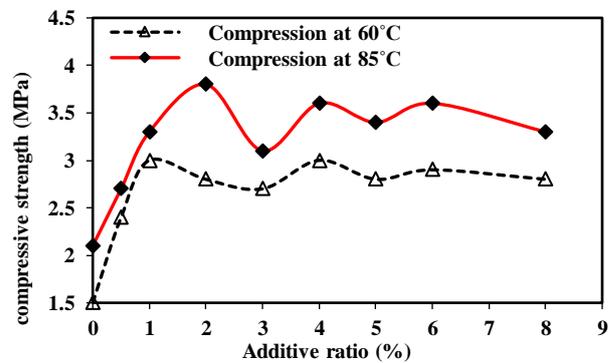


Fig. 8: The effect of aging on the compressive strength at different ratios of added white cement after 36 days at 60°C and 85°C.

physical properties with time at relatively high temperatures (60°C and 85°C). Practically, there is no decrease in both hardness and compressive strength with time for suggesting the kinetics model due to the curing of the gypsum. In other words, this phenomenon can be attributed to that the gypsum at this period is still at the curing state. Therefore, the effect of the presence of the additive on aging was investigated after 36 days as shown clearly in Figs. 7 and 8. It is apparent from those Figs. that the presence of the additive at the selected ratio (4%) has a positive effect on the shelf life of construction gypsum. It should be noted that gypsum is already added in a ratio of 3-4% to the powdered clinker in the cement industry mainly for improving the setting time of ordinary cement [27].

The aging study was also achieved in terms of the solubility in water at 55°C and 80°C (Table 4). The results listed in Table 4 show there is an equilibrium state in water solubility at 55°C. Such a phenomenon of equilibrium could be detected from the amount of dissolved material

does not increased with time in contrast to that at 80°C as it is clearly shown in Table 4. The reason for the existence of such kind of equilibrium at 55°C may be related to that at this temperature the dissolved calcium sulfate may be returned again to the surface of cubic sample due to the relatively high surface area of about 150 cm² (5x5x5cm). While, at 80°C no such an equilibrium was found due to the relatively high temperature which could avoid the molecular interactions of dissolved gypsum with surface of the sample.

The solubility data at 80°C of Table 4 have been applied to kinetics models of first-, second- and zero-order for finding the best fitted model according to the value of square correlation coefficient (r^2). The results indicate that the data are obeyed to the zero-order kinetics model due to the highest r^2 as explained in Table 5. It should be noted that the relatively small differences in r^2 between kinetics models (Table 5) can be considered as a usual phenomenon because the present dealing is with the rate of solubility neither with that of chemical reaction. Indeed, the zero-order

Table 4: Amount of 4% (w/w) white cement to gypsum of 0.05x0.05x0.05m samples dissolved (g) in water with time noting that these weights are corrected in order to make the original weight of all cubic samples is equal to 135g.

| Time (day) | Dissolved (g) at 55°C | Dissolved (g) at 80°C |
|------------|-----------------------|-----------------------|
| 4 | 11.70 | 6.09 |
| 8 | 11.91 | 7.83 |
| 12 | 9.855 | 10.39 |
| 16 | 7.827 | 13.20 |
| 20 | 8.060 | 25.37 |

Table 5: Application of kinetic models to the solubility data of Table 4 at 80°C, where *a* is the original weight of the sample at zero time (135g) and *x* is the weight loss at time *t*.

| Order | Kinetic equation | r ² |
|--------|------------------------------------|----------------|
| First | $kt = \ln \frac{a}{a-x}$ | 0.883 |
| Second | $kt = \frac{1}{a-x} - \frac{1}{a}$ | 0.865 |
| Zero | $kt = x$ | 0.899 |

reaction model is quite compatible with the present case as the solubility depends on the interaction between the solvent molecules with the surface of cubic samples (4% w/w), as when the surface is occupied by reactant molecules the increase in concentration does not increase the rate of reaction. Hence, the fitted model is corresponding to the zero-order, one could apply this model to the average values of dissolved amount at 55°C (Table 4) in order to calculate the rate constant (*k*) of dissolving process at this temperature. Table 6 show the resulted kinetics data including the rate constants, the activation energy (*E[#]*) and the natural logarithm of the frequency factor (*lnA*) according to the following equations [31,33]. The results (Table 6) clearly show there is an increase in the rate of solubility by more than two folds due to increase in temperature from 55°C to 80°C. Indeed, this can be related to that the intermolecular forces which responsible for the solvation are thermodynamically controlled. Moreover, the activation energy value is within the specified range for the solvation process (31-35 kJ/mole) [35].

$$\frac{k^2}{k^1} = \frac{E^{\#}}{R} \left[\frac{1}{T^1} - \frac{1}{T^2} \right] \quad (6)$$

$$\ln k = \ln A - \frac{E^{\#}}{RT} \quad (7)$$

Hence, according to the kinetic data that listed in Table 6, one could calculate the rate constant at 25°C using Equation (7)

Table 6: Zero order rate constants, activation energy and natural logarithm of frequency factor (*lnA*) for the solubility aging of 4% (w/w) white cement to gypsum samples.

| Temp. °K | <i>k</i> g day ⁻¹ | <i>E[#]</i> kJ/mol | <i>lnA</i> g day ⁻¹ |
|----------|------------------------------|-----------------------------|--------------------------------|
| 328.16 | 0.425 | 34.861 | 11.921 |
| 353.16 | 1.050 | | |

Table 7: Thermodynamic parameters for the solubility of 0.05x0.05x0.05m cubic samples of 4% in water during the aging process at two different temperatures (30 and 55°C).

| Δ <i>S^o</i> J/mol °K | Δ <i>H^o</i> kJ/mol | Δ <i>G^o</i> kJ/mol | <i>K_{ws}</i> | Temp. °K |
|---------------------------------|-------------------------------|-------------------------------|-----------------------|----------|
| 2.619 | 15.434 | 14.64 | 0.0030 | 303.16 |
| 24.111 | | 7.522 | 0.0635 | 328.16 |

which gives a value of *k* equal to 0.0861 g/day. Then, the half-life (*τ_{1/2}*) can be estimated using this relation *τ_{1/2}*=*a*/*2k* which gives a value of 784.1 day that equal to 2.15 years which can be considered as a very long period in contrast to the absence of the white cement.

On the other side, thermodynamic study on the solubility issue of gypsum in water was also inspected. The equilibrium constant of solubility (*K_{ws}*) at 55°C is calculated from the amount dissolved in Table 4 after a period of 20 days using Equation 4. While, the *K_{ws}* at 30°C is taken from Table 3 for the ratio of 4% after 22 days. Table 7 lists the thermodynamic properties for the solubility at 30°C and 55°C. The change in both of enthalpy (Δ*H^o*) and entropy (Δ*S^o*) have been evaluated using the following equations, respectively [31, 33, 36-38].

$$\frac{K_{ws2}}{K_{ws1}} = \frac{\Delta H^o}{R} \left[\frac{1}{T^1} - \frac{1}{T^2} \right] \quad (8)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (9)$$

It is apparent from the data of Table 7 that the sign of Δ*G^o* is positive as the solubility of gypsum in water is not spontaneous due to the presence of 4% (w/w) white cement. The sign of Δ*H^o* also positive as the solubility is an endothermic process which increases with the increase in temperature. On the other hand, Δ*S^o* also positive as the randomness increases due to solubility of solid materials as well as Δ*S^o* increases with the increase in temperature [31]. In general, the relatively low values of Δ*G^o* and Δ*H^o* reflect the relatively weak intermolecular forces of molecular interactions in contrast to that of fixed chemical bonds [37].

Hence, the use of white cement as an additive for improving the gypsum at ratio of 4.0% (w/w) could be considered as the optimum item for this purpose due to its

essential advantages in contrast to that of other types of additives. For instance, Wittbold *et al.* [15] invented a method of improving the strength of gypsum board through a protective thin surface film using water soluble polyphosphate salts with starch in addition to boric acid, fibers and glycerin. In comparison, it is quite difficult to apply the latter method for internal walls and roofs of buildings in addition to the complication factor of these additives.

Basically, in construction field, it is quite easier to deal with volume rather than weight. This due to that the volume can be measured using any container that may be available around the building site in contrast to that of balance. Therefore, the densities of both gypsum and white cement were measured at their powder state in order to change the ratio from w/w to v/v. The results give that the densities of gypsum and white cement are equals to 0.896 and 0.801 g/cm³, respectively. Hence, the ratio of improved gypsum will be 4.5% (v/v) white cement to gypsum. Noting that, the ratio of v/v depends on the density and this property depends merely on the commercial source of those material and also on the packing conditions.

It should be noted that the amazing success of the present study in solving the actual problems of construction gypsum can be related to the dependence of the announced treatment on the basics of chemistry. This was recognized from that the gypsum molecules (CaSO₄.2H₂O) bind themselves using the hydrogen bonding of their water molecules (water of crystallization) rather than that of the common fixed bonds. Therefore, such kind of relatively weak interaction between molecules will make these molecules vulnerable to interact with the foreign water molecules. In other words, there is a kind of competition between the foreign water molecules of solution and those within the crystal lattice for the formation of a hydrogen bond which lead to the phenomenon of gypsum solubility in water. Moreover, such a weak interaction of hydrogen bonding has a relatively longest intermolecular distance which then decreases the hardness as the latter depending on the packing of molecules. Consequently, the problems of water solubility and low hardness could be solved by strengthening the binding between molecules through addition of substances of no using of hydrogen bond such as tricalcium aluminate and silicate which they exist in white cement. Indeed, the main advantages of the proposed method for improving the properties of gypsum in

comparison to other related works are: using only one component as an additive, eliminating all the weak points, the simplicity, and can be considered as a green process from the health and environmental aspects.

CONCLUSIONS

The present study recommends strongly the use of white cement as an additive to construction gypsum at a ratio of 4% (w/w) or 4.5% (v/v) for treating the disadvantages in the field of building. Indeed, the developed gypsum due to presence of the suggested additive makes the employment of gypsum as the most favourite option with no comparable alternative material from health, environmental and economic point of view. Interestingly, the use of white cement as an additive (4.0% w/w) is not just restricted for eliminating the weak points of gypsum including the water solubility and the relatively low hardness, but it is expanding in the improvement of the related important properties such as the compressive strength and setting time. Actually, there are essential signs that may support the success of the present study which they are realized from the characteristics of the suggested additive including availability, inexpensive, healthy, no colouring, odourless, no volatile organic compounds (VOCs), used in very few ratio of 4% (w/w), and easy to deal with. Finally, the achievement of this study could be considered as an important object for the gypsum industry in order to produce an improved gypsum of no practical negative aspects by the addition of 4% (w/w) white cement.

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