RESEARCH PAPER

Physico-Mechanical Properties of Organo-Modified Bentonite Reinforced Cement Mortars

A. Allahverdi[1,2*], Z. Padar[3] and M. Mahinroosta[4]

*ali.allahverdi@iust.ac.ir

[1] Research laboratory of Inorganic Chemical Process Technologies, School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran.

[2] Cement Research Center, Iran University of Science and Technology, Tehran, Iran.

[3] Research laboratory of Inorganic Chemical Process Technologies, School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran.

[4] Research laboratory of Inorganic Chemical Process Technologies, School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran.

Abstract: *It is demonstrated that the addition of organo-modified Na-bentonite (OMB) particles to Portland cement mortar can promote its physical and mechanical properties. A series of experimental works on some important physicomechanical properties of Portland cement mortars mixed with various dosages of hydrophobic OMB was performed. The obtained results confirm that the OMB provides a dense packing effect. An optimum replacement level of around 3.5% (by weight) at an increased water-to-cement ratio of 0.53 results in an almost 11.43% increase in 28-day compressive strength along with about 20.78 and 16.20% reductions in a total volume of permeable pore space and water absorption, respectively. Also, at the optimum replacement level, an increase of about 2.72% is taken place in dry bulk specific gravity.*

Keywords: *Organo-modified bentonite, Cationic surfactant, Portland cement, Compressive strength, Water absorption.*

1. INTRODUCTION

It is well known that the durability of cement-based materials largely depends on the possibility of penetration of hazardous ions into their porous microstructures with water as a medium [1]. Water absorption and durability of these materials strongly depend upon water-to-cement ratio. Practical values of this ratio are as high as 0.65 for workable concrete without water reducing agents [2]. For durability and practical applications, it is accepted that cement-based materials should possess low permeability [3]. Reducing the water absorption and penetration of concrete can minimize sulfate and chloride ion attack, thus increasing the durability of concrete structures [4,5]. These goals can be achieved by a promising solution and that is the contribution of lamellar clays in cementing materials. In the past decade, bentonite has gained momentum in concrete research as supplementary cementitious material [6-9]. The term bentonite is applied for clayey materials majorly composed of smectite group phyllosilicates, a group of expandable clay minerals with a broad extent of chemical compositions [10,11]. This group involves Ca/Na-montmorillonite, nontronite, saponite, beidellite, and hectorite [12]. The characteristics of bentonite materials, such as plasticity, swelling ability, cation exchange capacity, etc. depend on the quantity of smectite minerals in the bulk material, smectite species and on the exchangeable cations in the interlayer position [11]. The bentonite can only be considered to comprise of individual particles ready for reactions if the bonds bridging the layers are weakened to the extent of separation of the layers. This happens when a modifier, is introduced within the layers, causing a change in the charge of the molecules and a subsequent separation of the layers. For this reason, surface

modification of the clay particles using an organic agent is necessary to provide compatibility with the matrix. In which case, the clay is said to be organo-modified, becoming hydrophobic [13].

Recent research activities have proven that hydrophobic admixtures can effectively reduce the water absorption of cement mortar and concrete and hence reduce the diffusion rate of aggressive chemical liquids [14]. Kuo et al. [14] added organo-montmorillonite (OMMT) to cement mortar and showed that optimal dosage of OMMT micro-particles, less than 1%, gives higher compressive and flexural strengths and a lower coefficient of permeability for cement mortars. In a different work, Kuo et al. [15] used organo-modified reservoir sludge (OMRS) as a substitute for a portion of fine aggregates in cement mortars and found out that it could be possible to replace up to 30% by mass of fine aggregates by OMRS particles in a cement mortar for normal practice. Also, excellent water-proof cement mortar was achieved when the percentage of OMRS particles was within the range of 5-50%. In another study, Colston et al. [16] confirmed that the strengths and microstructure of cement paste could be improved due to the introduction of organo-clays. Therefore, it can be said that some lamellar solids may be used as reinforcements in cement mortars and concrete.

For the first time, in the present work, bentonite was firstly organo-modified by using three quaternary ammonium salts and then the effect of its various dosages on some important physicomechanical properties of cement mortar specimens including compressive strength, dry bulk specific gravity, the volume of permeable pore and water absorption was investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

Type V Portland cement (PC), in accordance with ASTM standard, was supplied from Tehran Cement Company. Its fineness and bulk density were 295 m^2 kg^{-1} and 3145 kg m^{-3}, respectively. The Bogue's potential phase composition of this cement (in wt.%) was C_3S-65.31, C_2S-18.15, C_3A-3.16, and C_4AF-13.37 (C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3). The siliceous quartz sand in accordance with standard DIN-EN 196-1 was utilized for the preparation of the mortar specimens.

The bentonite clay used in this investigation was provided by Iranian Poudrsazan Company. The clay was Na-bentonite with a cation exchange capacity (CEC) of 65 meq per 100 g. Table 1 gives the chemical compositions of both PC and bentonite.

Table 1. Chemical compositions of Portland cement and bentonite

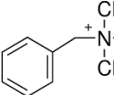| Oxide (wt.%)	Bentonite	PC
SiO_2	69.00	22.42
Al_2O_3	14.10	3.81
Fe_2O_3	0.70	4.20
CaO	1.12	64.90
MgO	2.52	0.08
SO_3	-	1.46
K_2O	0.10	0.42
Na_2O	3.50	0.22
Free CaO	-	1.07
LOI	8.90	1.61

Cationic surfactants including hexadecyltrimethyl ammonium bromide, dodecyl benzyl dimethyl ammonium chloride, and trioctylmethyl ammonium chloride as organo-modifiers were purchased from Sigma-Aldrich. Table 2 presents the main characteristics of surfactants. The surfactants were applied based on the long hydrophobic carbon chains attached to the central atom. It results in the increased surface area that will lead to better intercalation of organic cation between the layers of unmodified bentonite clay.

These surfactants are among quaternary ammonium salts which most often are used in organo-clay production. The optimum amount of surfactant for maximizing organo-clay hydrophobicity is reported to be in the range of 1 to 1.5 CEC of clay [16]. The same amount of each surfactant was first applied to determine the effectiveness of the selected cationic surfactants. Equation 1 was applied to calculate the required amount [16]:

$$a=[M(C/100)Mw]/(1000Q) \qquad (1)$$

where "a" is the amount of the cationic surfactant, C is the CEC value of the bentonite, M is the total weight of the bentonite, Mw is the molecular weight of the cationic surfactant and Q (here Q=1) is the number

Table 2. Main characteristics of surfactants

Surfactant	Molecular weight (g/mol)	Chemical structure	Purity (%)
Hexadecyltrimethyl ammonium bromide	364.45	$H_3C(H_2C)_{15}-\overset{\overset{\displaystyle CH_3}{\mid}}{\underset{\underset{\displaystyle CH_3}{\mid}}{N^+}}-CH_3 \quad Br^-$	≥98%
Dodecylbenzyldimethyl ammonium chloride	339.99	$\overset{\overset{\displaystyle CH_3}{\mid}}{\underset{\underset{\displaystyle CH_3}{\mid}}{\overset{+}{N}}}-CH_2(CH_2)_{10}CH_3 \quad Cl^-$	≥99%
Trioctylmethyl ammonium chloride	404.16	$CH_3(CH_2)_6CH_2-\overset{\overset{\displaystyle CH_3}{\mid}}{\underset{\underset{\displaystyle CH_2(CH_2)_6CH_3}{\mid}}{\overset{+}{N}}}-CH_2(CH_2)_6CH_3 \quad Cl^-$	≥97%

of valance electrons. The amount of surfactant calculated from equation (1) is equal to the number of exchangeable cations in the clay. When it is needed to add a higher amount of surfactant, the calculated value must be multiplied by a suitable coefficient. For example, to add 1.5CEC of cationic surfactant, the calculated value must be multiplied by 1.5.

2.2. Methods

2.2.1. Preparation of Organo-Modified Bentonite

Fig. 1 depicts the organo-modified bentonite (OMB) preparation steps. To prepare OMB, 500 mL deionized distilled water was poured into a glass container and 5 g of bentonite was then added slowly while stirring. The stirring was continued for at least 15 h at 70 °C for all platelets of the layered clay to be separated from each other for an effective cation-exchange reaction. Next,

the calculated amount of surfactant being dissolved in hot water was then slowly added to the bentonite suspension. The prepared solution was then stirred for an additional 24 h time period at 70 °C for the cation-exchange reaction to take place completely. The temperature and time values were recorded utilizing a temperature probe and an electronic time recorder, respectively.

The prepared OMB was filtered and washed for several times to remove all NaCl or NaBr salts and excess organic ions. To ensure the removal of NaCl or NaBr, a few drops of silver nitrate solution was added to the filtrate resulted from each try of washing. If bromide or chloride remains in the filtrate, the following reaction takes place:

$$AgNO_3 + Na(Br, Cl) \rightarrow NaNO_3 + Ag(Br, Cl)\downarrow \qquad (2)$$
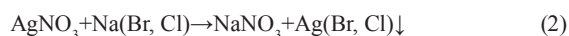
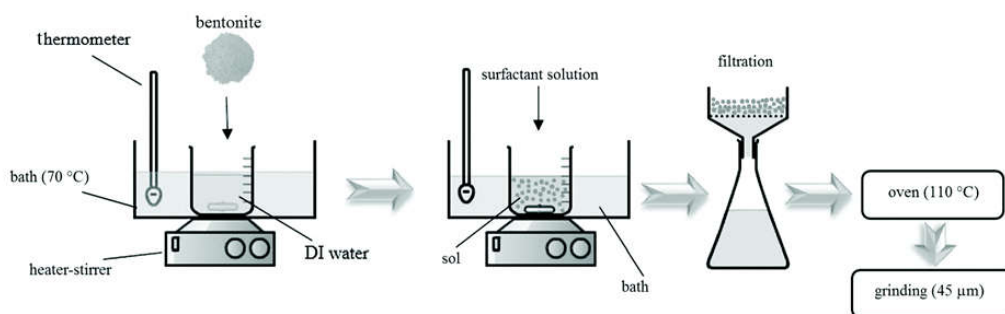The silver bromide or chloride precipitates in the aqueous environment, so washing is repeated

Fig. 1. Organo-modified bentonite preparation steps.

until the filtrate becomes transparent. It means all bromide or chloride has been removed from the clay. The OMB slurry was then dried at 110 °C for 48 h and ground into a fine powder of particle size less than 45 μm. This procedure was repeated using each of the above-mentioned cationic surfactants.

The organo-modification primarily takes place through cation exchange, replacing metal ions with organic cations. The adsorption of fatty surfactant molecules in the interlayer region of platy clay allows separation of the layers which promotes intercalation of polymer chains into the interlayer space [17]. The chemical structure of the OMB particles as schematically displayed in Fig. 2 shows that some absorbed water might be on the outer surfaces of silicate sheets and only a little water could exist in the interlayer regions between silicate sheets thru hydrogen bonding.
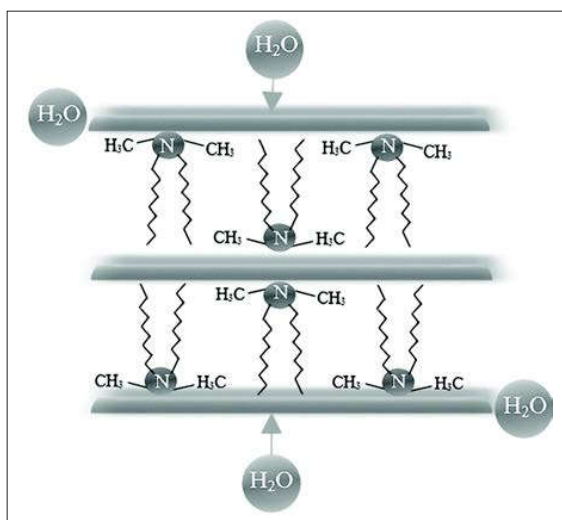

Fig. 2. A schema of the chemical structure of organo-modified bentonite particles.

2.2.2. Hydrophobicity of Bentonite Samples

To select a proper OMB sample, the evaluation of hydrophobicity is taken into consideration. For this reason, the contact angle was regarded and measured on each OMB samples. The results of contact angle measurements are shown in Table 3.

As it is obvious from Table 3, contact angle value for the OMB sample modified by hexadecyltrimethyl ammonium bromide is significantly less than two other values and therefore this cationic

surfactant was omitted from the work. Two other contact angles are quite close together and more detailed work was necessary to find their optimum amount and to judge about the suitable surfactant. For this reason, 0.50, 1.00, 1.25, 1.50, 1.75 and 2.00CEC of them were utilized to produce OMB samples. The obtained values of contact angles, shown in Figs. 3 and 4, verified that the OMB produced with 1.25CEC of trioctylmethyl ammonium chloride exhibits the highest hydrophobicity and this cationic surfactant, therefore, was chosen as the suitable modifier to produce enough OMB samples.
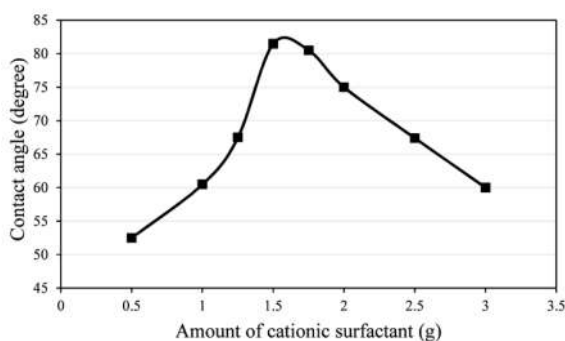

Fig. 3. Contact angle for bentonite modified with different amounts of dodecybenzyldimethyl ammonium chloride.
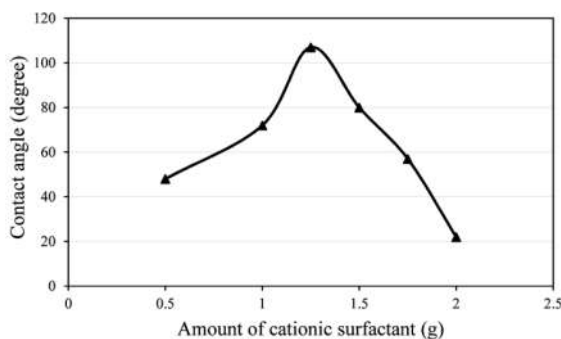

Fig. 4. Contact angle for bentonite modified with different amounts of trioctylmethyl ammonium chloride.

Fig. 5 shows typical images of water drops on not-modified bentonite (5a), bentonite sample modified with 1.5CEC of trioctylmethyl ammonium chloride surfactant with moderate hydrophobicity (5b) and bentonite sample modified with 1.25CEC of the same surfactant with superhydrophobicity (5c).

Table 3. Contact angle results for the organo-modified bentonite samples

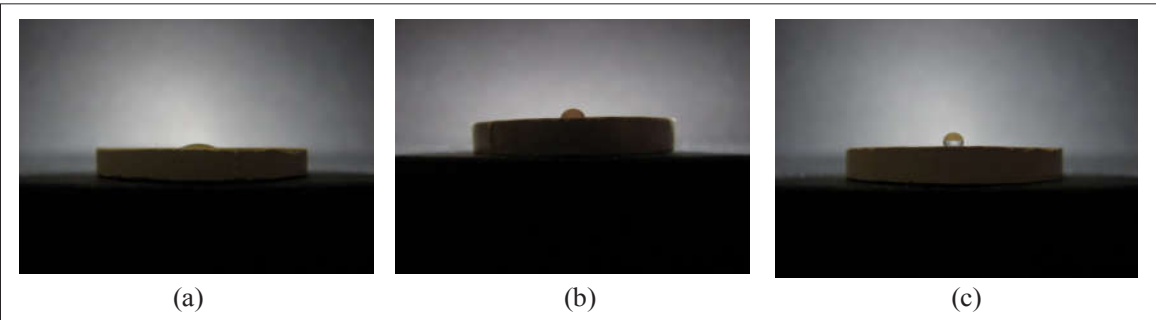| Modifier	Hexadecyltrimethyl ammonium bromide	Dodecylbenzyldimethyl ammonium chloride	Trioctylmethyl ammonium chloride
Contact angle (degree)	53.2	75.5	76.6

(a)	(b)	(c)

Fig. 5. Typical water drop images on (a) not-modified bentonite, (b) bentonite modified with 1.5CEC of surfactant, and (c) bentonite modified with 1.25CEC of surfactant.

2.2.3. Preparation of Mortar Specimens

To investigate the effect of the addition of the OMB on physicomechanical properties of Portland cement, the dosage of OMB expressed as weight replacement for cement was adjusted at 0, 0.25, 0.50, 0.75 and 1.00%. Enough 50 mm cubic mortar specimens were prepared in accordance with ASTM C109. The mortar specimens consisted of 1 part PC and 2.75 parts of sand proportioned by mass.

Since the OMB lowers the fresh mortar workability, the water-to-cement ratio (W/C) was adjusted for an approximately the same mortar workability determined by flow table test taking the flow as 110±5 % for fresh mortars in accordance with ASTM C1437 and ASTM C230. The adjusted water-to-cement ratios for different replacement levels are illustrated in Fig. 6.
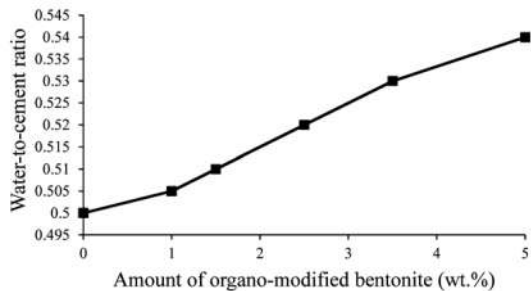

Fig. 6. Water-to-cement ratio for different replacement levels of organo-modified bentonite.

Mixing of OMB with cement is quite difficult due to its relative high specific surface area and its tendency to agglomeration. The mixing procedure of the constituents therefore greatly influences the properties of the cement mortar. For suitable mixing, the OMB was first mixed with enough amount of water in a closed container. The achieved suspension was stirred for about 20 h and at the same time, the pH value was adjusted between 3 and 4 [16] by adding 1 M phosphoric acid aqueous solution. After that, the other constituents including cement and sand were added slowly with complete mixing. The prepared cement mortars were then cast into molds. The molds were stored at an atmosphere of more than 95% relative humidity at 25 ºC for the first 24 h and then the specimens were cured in lime-saturated water at 25 ºC until the time of testing.

2.2.4. Measurement of Physico-Mechanical Properties

The physico-mechanical properties that are evaluated in the present study include compressive strength, dry bulk specific gravity, volume of permeable pore space, and water absorption. The effect of OMB dosage on compressive strength of Portland cement mortar specimens was investigated by measuring 7-,

14-, 21-, and 28-day compressive strengths. Equations 3 to 5 were also used to determine dry bulk specific gravity, volume of permeable pore space (voids), and water absorption of the mortar specimens in accordance with ASTM C 642-90:

Dry bulk specific gravity = A/(C-D) (3)

Volume of permeable pore space, % = (C-A)/(C-D) ×100 (4)

Water absorption after immersion, % = (B-A)/A×100 (5)

In which, A is the oven-dry mass; B is saturated mass after immersion; C is saturated mass after boiling, and D is immersed apparent mass. For each measurement, three specimens were used and the average value was reported as the result. The oven drying was carried out at 100 to 110 °C for not less than 24 h. After oven drying, the specimens were allowed to cool to ambient temperature and their masses were then measured. The oven drying was repeated until the difference between any two consecutive values was less than 0.5% of the lowest value measured. In the next step, the oven-dried specimens were immersed in water at 21 °C for not less than 48 h. After immersion, the surface of the specimens was dried with a towel to remove its surface moisture. The mass of the specimens (B value) was then determined. To obtain C value, the specimens were placed in a suitable container, covered with tap water, and boiled for 5 h. Afterward, the specimens were allowed to cool for not less than 14 h to a final temperature of 20-25 °C. After the temperature was achieved, the mass of the specimens was measured. In the final step, the specimens were suspended by a wire in water and their mass was determined (D value).

3. RESULTS AND DISCUSSION

3. 1. Compressive Strength

The results obtained for compressive strengths of mortar specimens are shown in Fig. 7. From the figure, it is seen that the 7-,

14-, 21-, and 28-day compressive strengths of mortar specimens increase initially and then decrease after reaching a peak value as the dosage of OMB enhances up to 5 wt.%. As seen, a replacement level of 3.5 wt.% can result in an almost 11.43% increase in 28-day compressive strength compared to plain PC mortar. The reason for the observed trend is that because the compressive strength is primarily controlled by the total porosity in mortars, the increase in compressive strength may probably be due to the reduction in total porosity (that will be confirmed in section 3.2). In addition, at relatively higher OMB replacement levels (beyond 3.5 wt.%), compressive strength undergoes a decrease accompanied with a decrease in dry bulk specific gravity and corresponding increases in both volume of permeable pore space and water absorption (to be considered in Figs. 8-10 in section 3.2) confirming the effect of excess OMB (more than 3.5%) in decreasing the compressive strength due to a reduction in microstructure compactness. One explanation for these observations might be the tendency of OMB to form clusters at replacement levels higher than 3.5 wt.%. This, in turn, can cause the enhancement of the volume of the permeable pore space and consequently decline of the compressive strength [13]. Detailed investigations are required to clear the exact mechanism of OMB on hydration kinetics and microstructure evolution of Portland cement paste that determine the concrete properties including compressive strength and porosity.
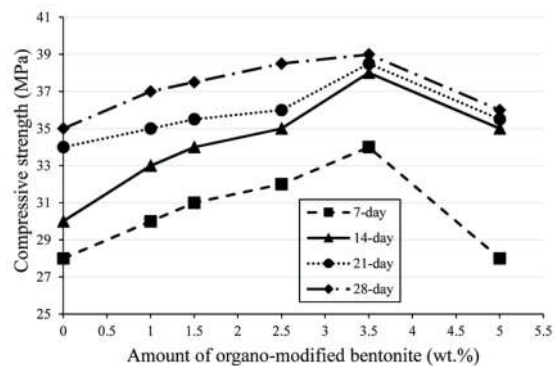

Fig. 7. Variations in compressive strength versus replacement level of OMB.

3. 2. Dry Bulk Specific Gravity, Voids, and Water Absorption

The results obtained for dry bulk specific gravity and volume of permeable pore space of 28-day cured mortar and paste specimens are shown in figures 7 and 8, respectively. A comparison of the results clearly shows reverse trends in variations of dry bulk specific gravity and volume of permeable pore space versus replacement level of OMB verifying each other. According to Figs. 8 and 9, at a replacement level of 3.5 wt.%, dry bulk specific gravity shows its peak value and volume of permeable pore space reaches its minimum value confirming the dense packing effect brought about by OMB. The variations observed in dry bulk specific gravity and volume of permeable pore space imply the presence of an optimum value around 3.5 wt.% for replacement level and at a water-to-cement ratio of 0.53 providing a dense packing effect. Effective modification of mortar properties by OMB, therefore, can result in an almost 20.78% reduction in the total volume of permeable pore space.
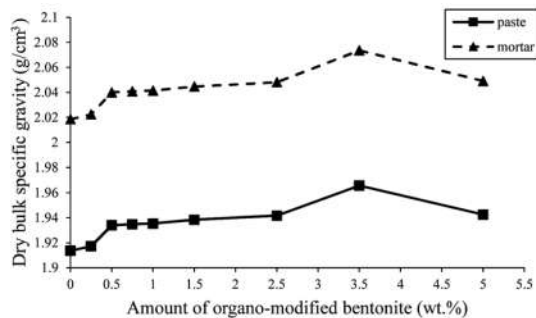

Fig. 8. Variations in dry bulk specific gravity of cement paste and mortar versus replacement level of OMB.
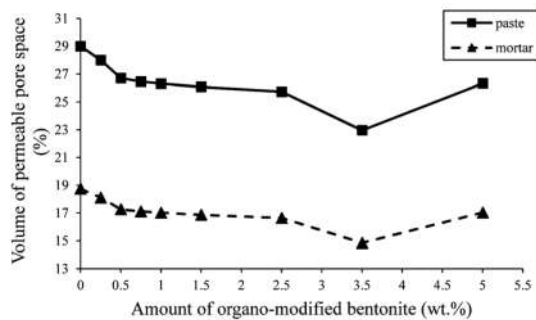

Fig. 9. Variations in volume of permeable pore space of cement paste and mortar versus replacement level of OMB.

The variations in water absorption caused by OMB are shown in Fig. 10. As represented by this figure, it can come to the conclusion that replacements at around 3.5 wt.% resulted in reduced water absorption. At this replacement level, the OMB particles situated around capillary pores can obstruct the diffusion of external solutions due to their hydrophobic properties. Therefore, an optimum replacement level can reduce the amount of water absorption by almost 16.20% compared to the reference mortar. Enhancement of the amount of water absorption at the replacement level of 5 wt.% is probably due to the formation of clusters of OMB around capillary pores. Formation of clusters can result in larger capillary pores which in turn increase the volume of permeable pore space and water absorption [2].
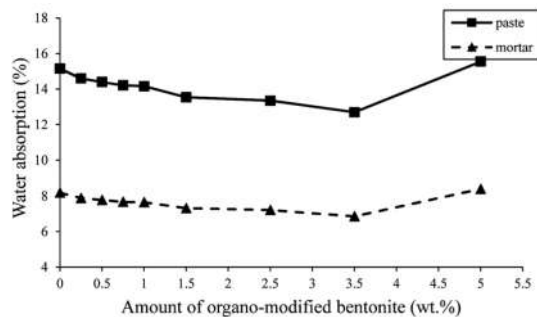

Fig. 10. Variations in water absorption of cement paste and mortar versus replacement level of OMB.

It should be noted that the price of the used surfactant, *i.e. trioctylmethyl ammonium chloride,* with a purity of more than 97% is 6-9 USD per gram [18], which can significantly affect the price of the final product. The important point, however, is the significant effect of which this has on durability performance and service life of the concrete structures in an aggressive environment. It must, therefore, be considered that the final product has great potential as a special concrete for special (and not general) applications. Studying the impact of the price of surfactant on the final product price is beyond the scope of this work because it requires a detailed and precise cost analysis including the concrete service life and the reduced repair costs during

the service life in aggressive environments compared to normal concrete.

In addition, utilization of OMB as a proper modifier of Portland cement mortar and concrete is at its very beginning stages to become an interesting research topic with great potential applications. This topic still requires much detailed basic research works on the effect of OMB on the rheology of fresh mortar and concrete, on the hydration kinetics of Portland cement phases and also on microstructure and porosity evolution.

4. CONCLUSION

In this study, the effect of various replacement dosages (0 to 5 % by weight) of Portland cement by hydrophobic organo-modified Na-bentonite (OMB) on some important physicomechanical properties of Portland cement mortars were presented. An optimum replacement level of 3.5 wt.% of OMB showed significant improvements in physicomechanical properties of Portland cement mortar including compressive strength, dry bulk specific gravity, volume of permeable pore space, and water absorption. At this replacement level, an almost 11.43% increase in 28-day compressive strength, 20.78% reduction in volume of permeable pore space, 16.20% decline in water absorption, and 2.72% enhancement in dry bulk specific gravity were observed. The obtained results aggregately propose the utilization of OMB as a proper modifier of Portland cement mortar.

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