Influencia de distintas fuentes de sílice en las propiedades físicas y mecánicas de materiales derivados del yeso

Effect of different forms of silica on the physical and mechanical properties of gypsum plaster composites

A. A. Khalil(*), A. Tawfik(*), A. A. Hegazy(*), M. F. El-Shahat(**)

RESUMEN

Se prepararon pastas compuestas de yeso y sílice mediante la mezcla en seco de yeso con distintas proporciones (0,2-10 %) de arena natural, o gel o humo de sílice, procediéndose a continuación a su hidratación. A fin de determinar las propiedades físicas y mecánicas de las pastas, a los 7 y los 28 días de hidratación se hallaron su fluidez, tiempo de fraguado, porosidad aparente, densidad aparente y resistencia a la compresión. Los resultados obtenidos indican que al incorporar las distintas modalidades de sílice a la mezcla, disminuyó la densidad aparente y aumentaron la fluidez, el tiempo de fraguado, la porosidad aparente y, en menor medida, la resistencia a la compresión de las muestras. Se considera que esta mejora de las propiedades del material se debe a la presencia de sílice en los poros intersticiales de las matrices endurecidas de yeso. Aunque la resistencia a la compresión de la mayoría de las pastas ensayadas apenas aumentó, estas se beneficiaron de la presencia en su composición de elementos de bajo coste como la arena o los distintos subproductos industriales utilizados. Puede concluirse, por lo tanto, que los compuestos de yeso y sílice tienen valor económico y contribuyen a mejorar el medioambiente al valorizar residuos. Por otra parte, son apropiados para las aplicaciones en las que se necesitan o recomiendan elementos de alta porosidad y bajo peso, concretamente en las edificaciones bajas.

Palabras clave: materiales compuestos, yeso, sílice, propiedades físicas y mecánicas, elementos constructivos.

ABSTRACT

Gypsum plaster/silica composites prepared by dry blending (0.2-10 %) natural sand, silica fume or silica gel and subsequently hydrated. Their physical and mechanical properties, including normal consistency, setting time, apparent porosity, bulk density and compressive strength, were determined after hydration for 7- and 28-days. The results indicated that adding different forms of silica lowered the bulk density and increased the normal consistency, setting time, apparent porosity and, to some limited extent, compressive strength of the composites. This improvement in properties can be attributed to the existence of silica in the interstitial pores in the hardened plaster matrices. While most of the composites revealed only scant rises in compressive strength, their composition was beneficial in so far as it included either a readily available low-cost constituent (sand) or industrial by-products. Consequently, the formed plaster-silica composites are of economic value, contribute to a cleaner environment by minimizing waste and can be used for applications where high porosity, lightweight units are required or recommended for low-cost buildings.

Keywords: *composites; gypsum plaster; silica; physical and mechanical properties; building units.*

(*) National Research Centre, Dokki (Giza, Egypt).
(**) Aim Shams Univ. (Cairo, Egypt).

Persona de contacto / *Corresponding author:* aakhalil100@yahoo.com

1. INTRODUCTION

The use of calcined gypsum has been known to humanity for so long that the date of the discovery of its properties is uncertain. The good condition even today of the indoor plaster in Ancient Egyptian pyramid stands as proof of that civilization's knowledge of its manufacture and use (1).

Vast high grade deposits of gypsum, the parent rock of plaster, outcrop in a number of places in Egypt (2, 3).Gypsum products such as plasterboard, gypsum blocks, gypsum tiles and self-levelling floor screeds, among others, are essential to all kinds of buildings. Offices, shops, and all manner of public buildings make substantial use of gypsum products (4, 5).Moreover, in recent decades gypsum products have been widely used as indoor surfacing. Homes, especially in the USA and Europe, are either made from or lined with gypsum-based products chosen by architects for their excellent properties, such as ready availability of inexpensive raw materials, volume stability, acoustic and thermal insulation, fire resistance, very low toxicity and the relatively low- energy and temperatures required in its manufacture (2).Gypsum is also used in many applications outside the construction industry: to make moulds for ceramic products (6), in medical (7) and dental supplements or implants (8), as a water conditioner for beer-brewing and sugar-refining, as an ingredient in flour, bread, ice-cream and pet food in addition to paper and pharmaceutical products. It is, moreover, an essential constituent in Portland cement, to retard its setting time (9). The various applications of gypsum plaster are based primarily on its specific properties (5, 10).

The use of neat (unblended) gypsum plaster entails a number of drawbacks, however. Relatively large amounts of mixing water may be needed, delaying setting time and lowering mechanical performance. Most gypsum plaster properties can be improved by including other constituents to form composites, i.e., a combination of two or more materials, one of which, the reinforcement, is in the form of fibers, sheets or particles embedded in the plaster matrix (11).

Several researchers have attempted to improve plaster properties and widen its range of applications by adding other materials (10, 12). Silica gel, a highly porous form of silica, is a by-product of the sodium silicate industry with excellent fire and heat resistance, along with chemical stability, a large specific surface area and high water sensitivity.In addition, its amorphous nature reduces density as well as thermal conductivity and enhances the high temperature durability of plaster composites with insignificant loss of compressive strength (5, 13).

The addition of nano-SiO_2 has been observed to increase the yield strength, modulus of elasticity (MOE) and Internal bond (IB) of plasterboard (14). Silica fume, in turn, is a very good pozzolan with a high reaction rate, although it is rarely used with gypsum (15). Several authors have reported that the addition of ultra fine sand (UFS) or micro-silica enhances the mechanical properties of Portland cement pastes (16, 17).

Hemihydrate hydrates and the water needed for setting (normal consistency, NC) comprises two types. The stoichiometric chemical demand of water, amounts to 18.6 ml per 100 g plaster, and that for workability (18). The amount used normally exceeds that minimum to facilitate workability, mixing or moulding. This practice usually leads to the generation of air voids and pores on drying, and decreases the mechanical strength of the hardened material (19). Other additives used to optimize plaster properties and widen its range of applications include vermiculite, silica fume and fly ash (10, 12-14).

Some of the disadvantages associated with gypsum products used for building purposes are low strength and water resistance (20). The present article studies the effect of adding different amounts of various forms of silica, namely natural sand, silica fume or silica gel, on the physical and mechanical properties of plaster composites to broaden their scope of application.

2. EXPERIMENTAL

2.1. Materials

The materials used in this study were industrial gypsum plaster, natural sand, silica fume and anhydrous silica gel. Gypsum plaster (gypsina) was provided by the Sinai gypsum company at Sinai, Egypt. The sand, a ball-milled natural rock, was supplied by Plena Group Co., Egypt while Sika Co., Egypt, supplied the silica fume. The chromatographic column silica gel used was manufactured by Merck, Darmstadt, Germany. Two sizes of natural sand were used by grinding separately and sieving to form fine ($\leq$90 µm) and ultra fine sand ($\leq$ 75 µm). The particle size of silica fume and silica gel was< 63 µm. The composition of the materials determined in a prior study showed that they are almost pure fine-grained materials with minor impurities (21).Plaster / silica composites were prepared by blending gypsum plaster with 0.2 to 10% of each form of silica for about 15 minutes. The physical and mechanical properties of the composites, including the normal consistency (NC), setting time (ST), apparent porosity (AP), bulk density (BD) and compressive strength (CS), were determined.

2.2. Methods

The physical and mechanical properties of the plaster / silica composites were determined according to ASTM

standard C 472 (22). NC and ST were determined using modified Vicat and Vicat apparatuses, respectively. The composite pastes, prepared by mixing the plaster/silica powders with their respective determined normal consistencies, were casted in steel cube moulds and stored in ambient conditions for 7 or 28 days for AP, BD and compressive strength testing.

AP and BD were determined using the liquid kerosene method and applying the mathematical equations mentioned in the literature (12, 23).

Compressive strength was determined using a universal testing machine and the applied load to each cube for rupture was recorded and divided by its surface area. The values reported for the samples are the mean of at least five measurements.

3. RESULTS AND DISCUSSION

3.1. Normal consistency (NC)

The results given in Table 1 express the volume of water needed as normal consistency (NC) for plaster composites from which it is clear that:

Table 1
Amount of water needed (ml water/100 g powder) to attain normal consistency in plaster composites containing natural sand, silica fume or silica gel

Addition, wt%	Fine sand	Ultrafine sand	Silica fume	Silica gel
0	60			
0.2	60	60	60	60
0.4	60	60	60	61
0.6	60	60	61	61
0.8	60	60	61	62
1	60	60	61	62
3	60	59	63	67
5	59	59	65	71
7	59	59	67	75
10	58	58	70	82

1. The NC value of 60% for neat plaster means that 60 ml of water is needed per 100 g of plaster to attain standard normal consistency. The addition of up to 3% of natural sand unaffected that value. Larger proportions (5%–10%) of fine sand, however, apparently lowered the NC of the composites. Although sand is known to be a non-hydraulic additive that requires some water to wet the surface of the grains when added to plaster, it also dilutes its content. That in turn lowers the water demand of the blend and increases the amount of water available for workability. These two phenomena intensify with increasing sand content. Addition

of 10% sand, for instance, dilutes the plaster content to 90% and reduces its NC to 54 ml of water/100 g composite. At the same time, however, the added sand slightly increases the NC of the composites because of the extra water needed to wet its grains. The difference between the calculated NC (58 %) for the composite and the water needed for normal consistency of its plaster (54%) so 4% will stay free and some of which is used to wet the sand grains while the rest enhances the workability of the composites.

2. The water required to attain normal consistency in the plaster composites containing ultrafine sand was almost similar to that for the fine sand composites, despite the higher surface area of the former (13.34 compared to 10.38 m^2/g), which would need more water to wet the sand grains (21). The inference is that surface area insignificantly affects the amount of water adsorbed onto sand grains in the range of the studied particle sizes.

3. Minor additions of either silica fume or silica gel slightly increased the NC of their composites, due to the extra water required to wet their larger surface areas (21). Moreover, their surface areas are much greater than those of natural sand which increased the amount of water required as normal consistency of either of them. Larger replacement ratios of silica fume or silica gel increased the NC of the composites.

4. The NC of the silica gel composites also is high, particularly with increasing replacement ratios, due to the high moisture affinity of the gel and its comparatively large surface area (5, 21).

5. The NC ranking for the studied additives is: natural fine sand <ultra fine sand < silica fume < silica gel.

3.2. Setting time

The setting time results of the studied materials are given in Table 2 from which it is clear that:

1. Setting time depends on the binder/filler ratio; the lower the ratio, the longer the setting time. Filler surface area plays an important role in the setting mechanism because larger surface area increases the ability of the filler to spread and delay the bonding and interlocking of gypsum crystals.

2. The initial setting time of neat plaster was observed to be short, while the final time was almost twice the initial time. The setting time was almost higher in plaster/sand composites than in the neat plaster and gradually increased with increasing sand replacement ratios. That is consistent with the increase in the workability water in the sand composites, given that excess water is known to retard setting time of plaster (12).

3. Higher proportions of both forms of sand lengthened the setting time of the formed composites.

Table 2
Setting times for plaster composites containing natural sand, silica fume or silica gel.

Additive	Fine sand				Ultra fine sand				Silica fume				Silica gel			
	Initial Set		Final Set		Initial Set		Final Set		Initial Set		Final Set		Initial Set		Final Set	
Wt%	min	Sec	min	Sec	min	sec	min	sec	min	Sec	min	sec	min	sec	min	Sec
0	8	30	15	00	8	30	15	00	8	30	15	00	8	30	15	00
0.2	8	26	14	11	8	12	15	12	9	30	17	8	10	13	15	13
0.4	8	27	14	14	9	20	15	9	10	12	17	14	11	00	15	30
0.6	8	26	13	23	9	21	15	15	11	8	18	00	12	15	17	00
0.8	8	25	13	19	9	23	15	13	12	30	20	12	13	30	19	30
1	8	30	12	30	10	00	16	00	14	00	22	11	13	11	20	8
3	9	13	13	00	12	30	18	13	14	15	22	13	13	14	21	12
5	9	21	13	30	13	11	22	20	14	16	22	14	14	11	22	00
7	11	30	17	13	15	00	23	12	14	18	22	30	15	00	25	13
10	12	00	16	30	16	15	23	17	14	15	23	11	17	11	28	12

4. Setting time was retarded much more significantly in the plaster containing ultra fine sand than in the fine sand composites. This result is also consistent with the NC findings, for the values of the ultra fine composites which are lower than the fine sand composites; both are lower than neat plaster.

5. Silica fume retarded the setting time of the plaster/ fume composites due to its higher NC values, more intensely with rising replacement ratios.

6. The composites containing silica gel exhibited the longest setting times, in as much as their NC values were higher than the observed for the other silica composites. The setting time of the plaster/gel composites clearly increased with higher gel contents.

7. By setting time, the composites studied ranked as follows: fine natural sand < ultra fine sand< silica fume < silica gel.

3.3. Apparent porosity and bulk density

The apparent porosity and bulk density of the composites tested are shown in Tables 3 and 4and graphically in Figures 1-4 and 5-8, respectively. The findings are discussed below:

1. Seven-day neat plaster gave moderately porous, moderately dense matrices, as a result of the generation of air bubbles trapped during mixing and the evaporation of the excess water needed for workability. Water evaporation increased porosity and reduced the BD of the hardened material.

2. Adding sand slightly reduced 7-day porosity and yielded denser matrices. As a fine-particle material the sand very likely filled the interstitial spaces in the plaster-sand composites. With small replacement ratios (up to 1%) of natural sand, the BD of the 7-day composites remained essentially unaltered, because while sand is denser than plaster, more water was required to attain a normal consistency for these composites than neat plaster. In other words, these two effects off set one another, so that as the proportion of sand increased, the larger amount of workability water limited its greater density from affecting the BD of the end product.

3. The BD of the plaster / sand composites is the result of the combined densities of its four main constituents: plaster ($\approx$ 2.2 g/cm^3), water (1 g/cm^3), sand (>2.5 g/cm^3) and open air-filled pores (< 1 g/cm^3), according

Table 3
Apparent porosity (AP, %) of 7- and 28-day plaster composites containing natural sand, silica fume or silica gel.

Addition, wt%	Fine sand		Ultra fine sand		Silica fume		Silica gel	
Age, days	7	28	7	28	7	28	7	28
0	40.68	39.25	40.68	39.25	40.68	39.25	40.68	39.25
0.2	40.60	39.11	40.9	40.54	36.55	36.1	39.56	36.9
0.4	40.54	39.05	41.22	40.22	37.00	35.7	39.48	38.4
0.6	40.48	38.95	41.56	39.85	37.55	35.3	39.37	37.7
0.8	40.44	38.88	41.8	39.44	38.19	35.0	39.45	37.9
1	40.42	38.84	41.91	39.28	38.19	34.6	44.64	39.5
3	40.03	37.63	41.00	38.94	39.00	34.5	45.00	40.7
5	39.89	36.44	39.22	38.97	41.16	36.6	45.65	41.9
7	39.55	36.22	39.15	38.76	43.00	37.6	47.52	45.7
10	36.49	35.31	40.13	39.38	45.05	37.1	49.94	48.5

Table 4
Bulk density(g/cm^3) of 7- and 28-day plaster composites containing natural sand, silica fume or silica gel.

Additive, wt%	Fine sand		Ultra fine sand		Silica fume		Silica gel	
Age , days	7	28	7	28	7	28	7	28
0	1.16	1.15	1.16	1.15	1.16	1.15	1.16	1.15
0.2	1.16	1.15	1.15	1.12	1.16	1.14	1.14	1.14
0.4	1.16	1.15	1.15	1.12	1.15	1.14	1.13	1.13
0.6	1.16	1.15	1.15	1.12	1.15	1.13	1.10	1.09
0.8	1.16	1.15	1.15	1.12	1.14	1.13	1.08	1.06
1	1.15	1.15	1.15	1.12	1.13	1.12	1.09	1.06
3	1.16	1.13	1.15	1.15	1.10	1.10	1.06	1.04
5	1.13	1.15	1.16	1.16	1.08	1.08	1.02	1.03
7	1.11	1.13	1.17	1.16	1.09	1.05	0.99	0.99
10	1.01	1.13	1.16	1.16	1	1.03	0.94	0.95
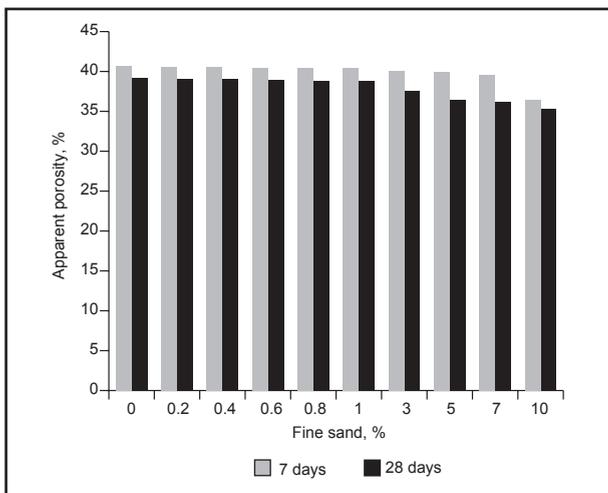
Figure 1. Apparent porosity (AP, %) of 7- and 28-day plaster/ fine sand composites.
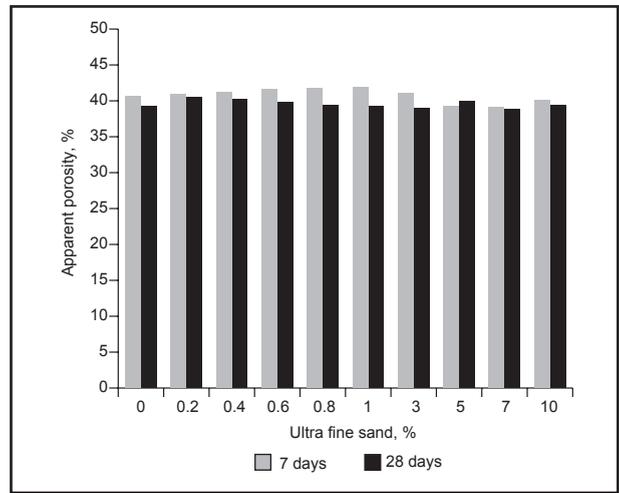
Figure 2. Apparent porosity (AP, %) of 7- and 28-day plaster/ ultra fine sand composites.
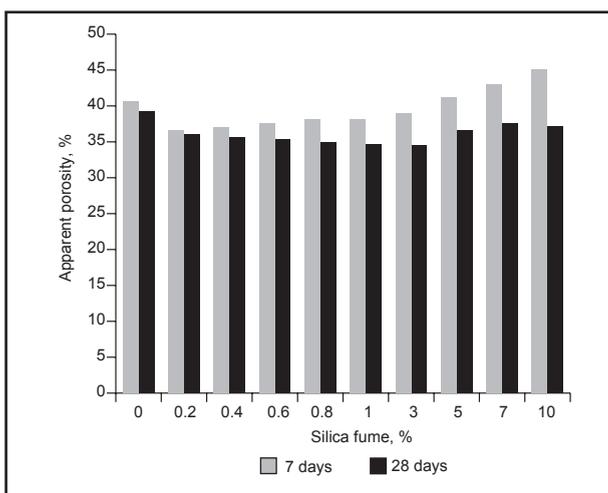
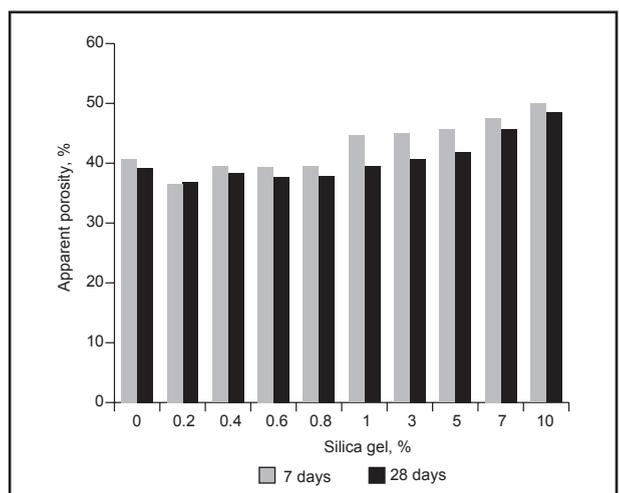Figure 3. Apparent porosity (AP, %) of 7- and 28-day plaster/ silica fume composites.

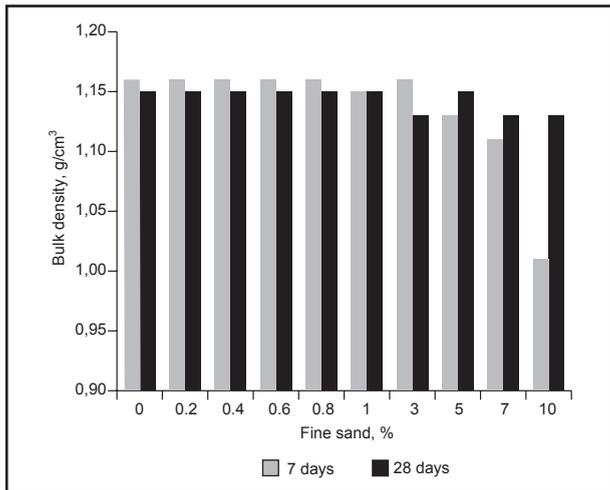Figure Apparent porosity (AP, %) of 7- and 28-day plaster/silica gel composites.

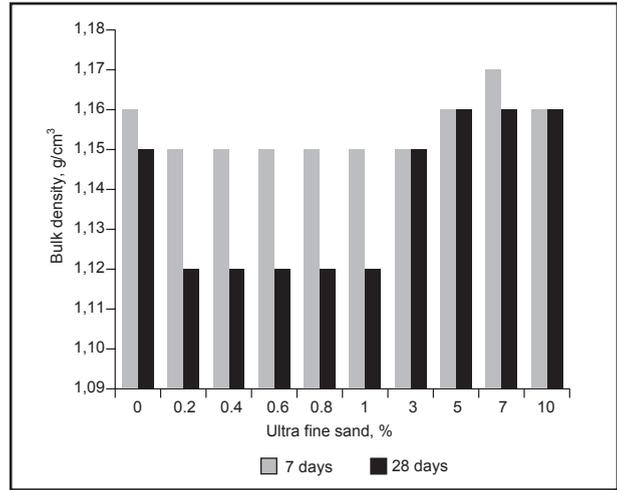Figure 5. Bulk density of 7- and 28-dayplaster/fine sand composites.

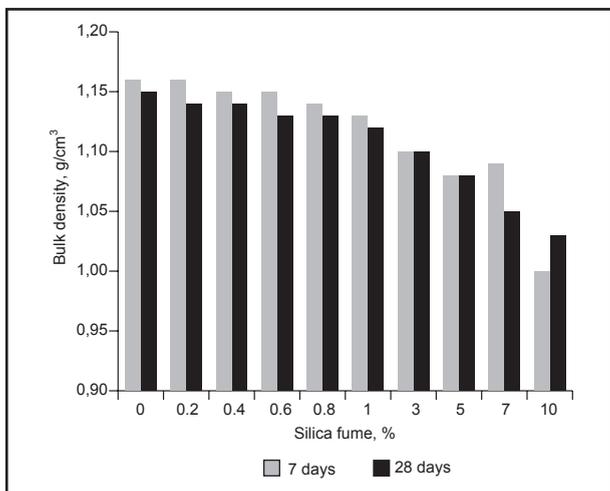Figure 6. Bulk density of 7- and 28-dayplaster/ ultra fine sand composites.

Figure 7. Bulk density of 7- and 28-day plaster/ silica fume composites.
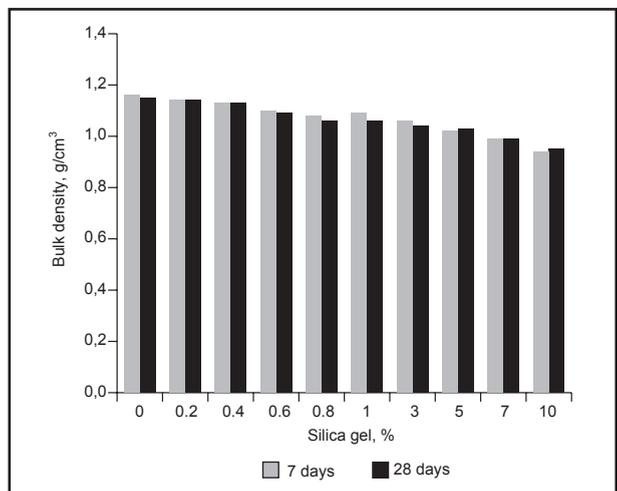

Figure 8. Bulk density of 7- and 28-day plaster/silica gel composites.

to the content of each in the composite. Excess water would raise composite porosity and decrease its bulk weight and density. Increasing the water and/or pore content would at least partially offset the effect of the higher density of sand in the composites.

4. The BD values were almost the same for the fine sand and ultra fine sand composites, except at the higher replacement ratios, where BD was higher in the ultra fine composites. This was attributed to the difference in the porosity ratios.

5. The AP values of the plaster / silica fume or plaster / silica gel composites with low silica contents (up to 1%) were slightly lower than neat or sand- plaster composites. When higher percentages (3% -10%) of addition were used, the composites exhibited high porosity due to the evaporation inherent in their higher NC values. Determined under similar conditions,

apparent porosity of silica fume composites (containing small percentages) was slightly lower than those containing either sand or silica gel. This may be due to the extreme fineness of silica fume, which would enable it to fill more of the interstices between the grains of hardened plaster.

6. Adding silica fume or silica gel to gypsum plaster slightly lowered the bulk density of the 7-day composites. This decrease was intensified with high additive content. As mentioned above, these composites lowered the AP of neat plaster by filling the interstitial spaces between the plaster grains, although due to their higher NC, at higher replacement ratios they proved to be more porous than neat plaster. Under such conditions (proportions up to 10%), BD is logically declined.

7. Silica gel, with the highest NC also exhibited the highest porosity.

8. With increasing percentages of silica forms, the AP values increased and BD declined due to the extra water needed for workability, which induced higher porosity during drying and curing.

9. Porosity was greater and density lower in the 28-day than in the 7-day composites. As more water evaporated, the porosity of the hardened plaster composites was increased, reducing its bulk weight and left its bulk volume insignificantly changed; BD consequently declined slightly. The rise in AP in all the studied composites intensified with rising additive content. Moreover, the water added to enhance both plaster and silica workability evaporated on curing, with insignificant rise in porosity.

10. By AP, the studied composites ranked as follows: silica fume > silica gel> natural sand.

3.4. Compressive strength (CS)

The CS results for the plaster composites are given in Table (5) and graphed versus hydration time in Figures 9-12. These findings are discussed as:

1. Gypsum plaster is known to set when its hydrated crystals bound and interlock to form the hard mass. The presence of a filler physically separates the hydrated crystals, inducing imperfect bonding.

2. Seven-day neat plaster exhibited moderate compressive strength. The strength of composites of the same age containing small amounts (up to 3%) of fine sand was insignificantly differ from neat, even though these composites accommodated higher normal consistency than neat counter part. When 5 % of fine sand was added, the compressive strength of the composite increased, whereas composites containing higher proportions (7% and 10%) of sand gave lower strength values than either neat plaster or those composites with replacement ratios of 5% or below.

3. Fine sand grains are assumed to enhance plaster compressive strength by occupying the interstitial pores in the hardened matrix. As noted earlier, however, such additions entail a slight increase in the NC. The excess water would reduce the compressive strength of the composites (19). The net result of these two opposing phenomena was the scant difference in the plaster/fine sand composite or neat plaster.

4. The use of a higher sand content led to even greater water of workability in the NC values, which separated the crystals in the hardened plaster, i.e. increased porosity which led to decrease compressive strength.

5. Compressive strength of the ultra fine sand composites was almost higher than either neat plaster or plaster / fine sand composites. Strength increased with increasing ultra fine content up to 5%, and subsequently declined. Adding 7% or 10 % ultra fine sand gave lower CS than the 5% samples, but still higher than that observed in neat plaster. With its smaller particle size, the ultra fine sand could more readily fill the interstices in the plaster matrix than the fine sand did.

6. Adding silica fume or silica gel reduced the CS of their respective 7-day composites. The intensity of this effect increased with the increased silica content as a result of the excess water needed to reach normal consistency. Moreover, some of this excess water was retained in the matrix even after 7 days due to the hygroscopic nature of both types of silica forms.

7. The effect of added silica on the compressive strength of plaster composites varied with the form of silica used. The most significant effect was observed for sand, despite the finer particle size of the other additives. This indicates that the effect is due to the presence of silica grains in the interstitial voids in hardened plaster matrixes rather than of the possible formation of new compounds. As sand grains are harder than either silica fume or silica gel particles, the plaster/sand composites showed higher strength than either silica fume or silica gel composites.

8. With nearly all the additives, strength increased with curing time, because after 28 days the hydration reactions had run through to completion and the residual water had almost evaporated.

Table 5
Compressive strength (MPa) of 7- and 28-day plaster composites containing natural sand, silica fume or silica gel.

Addition, wt%	Fine sand		Ultra fine sand		Silica fume		Silica gel	
	7 days	28 days	7 days	28 days	7 days	28 days	7 days	28 days
0	12	15	12	15	12	15	12	15
0.2	12	14	12	14	10	12	11	12
0.4	12	14	12	14	11	13	12	13
0.6	11	15	12	14	11	14	13	13
0.8	11	15	12	14	11	14	13	13
1	11	15	12	14	13	16	14	14
3	12	15	14	14	9	14	13	11
5	12	15	14	15	9	13	11	9
7	10	13	13	14	8	11	10	7
10	9	13	13	14	7	11	8	8

Figure 9. Compressive strength (CS) of 7- and 28-day plaster / fine sand (< 90 micron) composites.

Figure 10. Compressive strength (CS) of 7- and 28-day plaster / ultra fine sand (< 75 micron) composites.
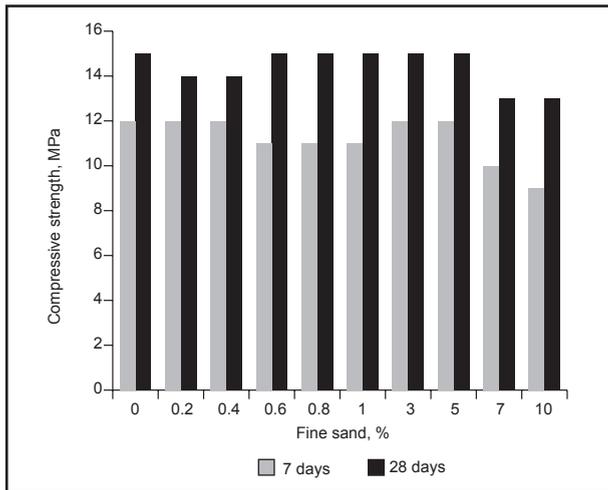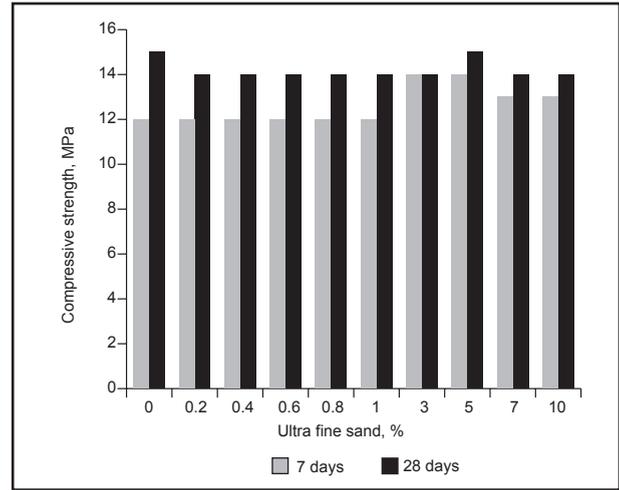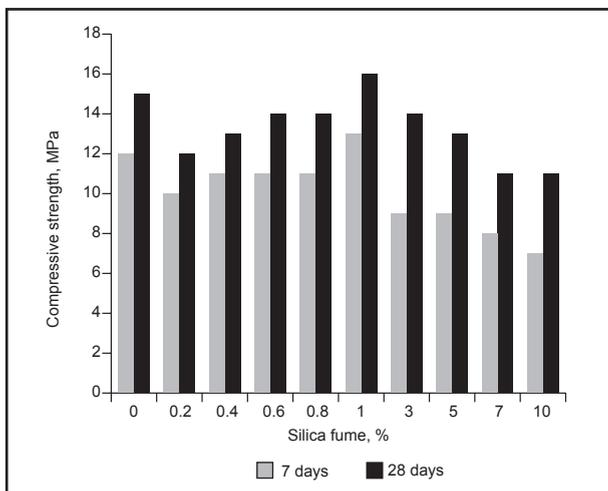

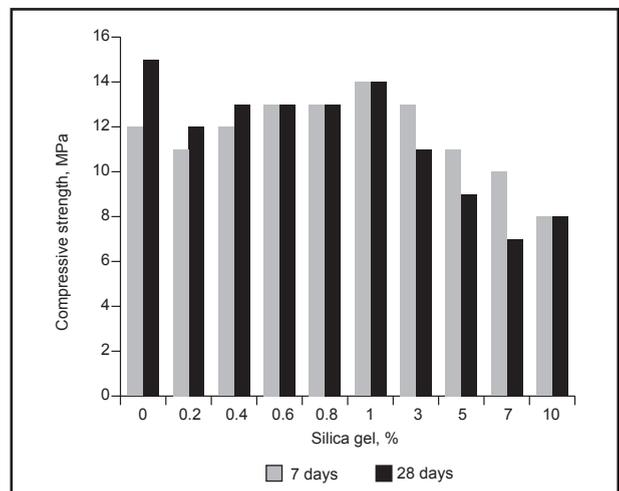Figure 11. Compressive strength (CS) of 7- and 28-day plaster /silica fume composites.

Figure 12. Compressive strength (CS) of 7- and 28-day plaster / silica gel composites.

4. CONCLUSIONS

a) Gypsum plaster/silica composites were formed by blending plaster with various percentages of diffe-rent forms of silica.

b) The addition of up to 5 % fine sand and of nearly all the studied percentages of ultra fine sand induced a slight re-duction in bulk density and the amount of water needed for normal consistency in the composites, while increa-sing their apparent porosity and compressive strength.

c) Bulk density declined in all the composites and the neat plaster and their strength and porosity increa-sed between 7 and 28 days as a result of the com-pletion of the setting process and the evaporation of almost retained water.

d) The mechanism involved in the improvement of plaster properties was physical: namely, the filling of the interstitial pores in the hardened plaster matrixes. This effect varied depending on the form of silica used. The most significant difference with the neat plaster was observed in the composites containing sand, although the other forms had finer particles. This stands as proof that the effect was due to the interstitial presence of the grains in the hardened plaster matrix rather than to the possible formation of new compounds. Since sand grains have a harder consistency than silica fume or silica gel particles, their plaster composites exhibited higher strength than either silica fume or gel..

e) Plaster/silica composites are consequently suitable for a number of applications, such as in non-concrete low-prise buildings where lightweight, high-porosity units are recommended.

REFERENCES

(1) McDowell, S.J. "Development of Proposed Standards and Tests for Plaster of Paris in Ceramic Industries" *Bull. Am. Cer. Soc.* 14 (1935) 229-235.

(2) Khalil, A.A.; Gad, G.M. "Mineral and chemical constitutions of the UAR gypsum raw materials". *Indian Ceramics*, 16 (1972) 173 - 177.

(3) Said, R. "The Geology of Egypt" A. A.Balkama , Rotterdam (1990).

(4) Gartner, E M: "Cohesion and expansion in polycrystalline solids formed by hydration reactions: The case of gypsum plasters". *Cem. Concr. Res.* 39 (2009) 289–295. http://dx.doi.org/10.1016/j.cemconres.2009.01.008

(5) Bas_pinar, S. M.; Kahraman, E. "Modifications in the properties of gypsum construction element via addition of expanded macroporous silica granules". Construction and Building Materials 25 (2011) 3327–3333. http://dx.doi.org/10.1016/j.conbuildmat.2011.03.022

(6) Combe, E. C.; Smith, D. C. "Some Properties of Gypsum Plaster" . J. Brit. Dent., 17 (1964) 237-245.

(7) Peters, C. P.; Hines, J. L.; Bachus, K. N.; Craig M. A.; Bloebaum, R. D. "Biological Effect of Calcium Sulfate as Bone Graft Substitute in Ovine Metaphyseal Defects" J. Biomed. Mater. Res. A., 76, No3 (2005) 456-462

(8) Craig, R. G. "Restorative Dental Materials" 7th Edition, St. Louis, Toronto, and Princeton. The C.V. Mospy comp., (1989) 303-330.

(9) Papageorgiou, A.; Tzouvalas, G.; Tsimas, S. "Use of Inorganic Setting Retarders in Cement Industry" *Cem. Concr. Res.*, 27 (2005) 183-189. http://dx.doi.org/10.1016/j.cemconcomp.2004.02.005

(10) El-Maghraby, H.F.; Gedeon, O.; Khalil, A.A. "Formation and Characterization of Poly(vinyl alcohol – co – vinyl Acetate – co-itaconic Acid/ Plaster Composites: part II: Composite Formation and Characteristics" *Ceramic Silikaty* 51, nº 3 (2007) 168-172.

(11) Arikan, M.; Sobolev, K. "The Optimization of Gypsum Based Composite Material" *Cem. Concr. Res.*, 12 (2002) 1725-1728. http://dx.doi.org/10.1016/S0008-8846(02)00858-X

(12) Khalil, A.A.; Abdel kader, A. H. "Preparation and physicomechanical Properties of Gypsum Plaster-Agro FiberWastes Composites" Interceram Int. J. Refractories Manual (Special Technologies) 21 (2010), 62-67.

(13) Murat, M.; Attari, A. "Modification of some physical properties of gypsum plaster by addition of clay minerals", *Cem. Concr. Res.,* 2 (1991) 378–87. http://dx.doi.org/10.1016/0008-8846(91)90019-E

(14) Wen, L.; Yu-he, D.; Mei, Z.; Ling, X.; Qian, F. "Mechanical properties of nano SiO_2 filled gypsum particle board" *Trans Nonferrous Metals Soc China* 16 (2006), 361-364. http://dx.doi.org/10.1016/S1003-6326(06)60210-0

(15) Fu, X.; Chung, D.D.L. "Effects of silica fume, latex, methylcellulose, and carbon fibers on the thermal conductivity and specific heat of cement paste." *Cem. Concr. Res.*, 27, nº 12 (1997), 1799-1804. http://dx.doi.org/10.1016/S0008-8846(97)00174-9

(16) Shebl, S.S.; Seddeq, H. S.; Aglan, H. A. "Effect of micro-silica loading on the mechanical and acoustic properties of cement pastes" Construction and Building Materials 25 (2011), 3903-3908. http://dx.doi.org/10.1016/j.conbuildmat.2011.04.021

(17) Ogawa, K.; Uchikawa, H.; Takemoto, K.; Yasui, I. "The mechanism of the hydration in the system C_3S- pozzolana", *Cem. Concr. Res.*, 10 (1980) 683-696. http://dx.doi.org/10.1016/0008-8846(80)90032-0

(18) Khalil, A.A. "Gypsum Plaster: II-Constitution and Properties of the Prepared β-Hemihydrates" *J. Appl. Chem. Biotechnol.* 22, nº 6 (1972), 703-709. http://dx.doi.org/10.1002/jctb.5020220609

(19) Khalil, A. A.; Saniour, S.H. "Characterization of the prepared dental gypsum plasters" *Interceram* 46, nº 4, (1997) 250-253.

(20) Ohama, Y.; Oikawa, K.; Terata, O. "Process Technology of Polystyrene Gypsum Mortar Systems" *Proc. Jpn. Congr. Mater. Res.,* 22 (1979), 348-351.

(21) Khalil, A.A.; Tawfik, A.; Hegazy, A. A.; El-Shahat, M. F. "Gypsum plaster composites: I-Characterization of the starting materials" Egypt. *J. of Appl. Sci.* ISSN 1110-1571, 27, nº 9 (2012), 746-760.

(22) ASTM, Standard Methods for Physical Testing of Gypsum, C472-99(2009).

(23) Khalil, A.A.; Mohamed, A.I. "Firing Characteristics, phase composition and physicomechanical properties of Tushka Clay bodies fired at different temperatures" *Interceram* 60, nº 1, (2011)20-24.