Contribution of Economic Nano-materials and Industry By-Products to the Fresh and Hardened Properties of Cement Mortars

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Abstract

This study aims at evaluating the influence of low cost nano materials including: nano silica (NS) and nano clay (NC) and various industry by-products including; silica fume (SF), Fly ash (FA), and fine Air-Cooled Slag (FACS) as cement replacements on the compressive strength, flexural strength and rheological properties of cement mortars. The results revealed that, the investigated industrial by-products contribute to the strength development by various ratios at various replacement percentages. The best mechanical performance was obtained for the mortar incorporating 15 wt. % SF; remarkable enhancements by about 30.8 and 26.8 were obtained for the compressive and flexural strengths respectively as compared with the plain ordinary mortar. FACS showed insignificant contribution to both compressive and flexural strengths. Even at low levels of replacement; the nano-materials provide better enhancements of the mechanical strength. Incorporation of 3 wt. % NS into the cement mortar has increased the compressive strength by about 38.5%; while, the incorporation of 5 wt.% of activated NC has considerably increased the flexural strength by 59% as compared to the ordinary cement mortar at 28 days of hydration. The workability of the blended mortars decreases with the loading of silica fume, fine air cooled slag nano-silica and nano-clay while increases with using fly ash and marble dust. The nano materials showed noticeable improvement of the structural integrity and microstructure, confirming the enhanced durability characteristics.

Keywords: Cement mortar, industry by-products, nano-silica, nano-clay, compressive strength, flexural strength, microstructure

I. INTRODUCTION

Globally, management of solid wastes poses a herculean challenge to developed and developing countries owing to industrial growth, construction booms, rapid urbanization, and consumeric lifestyle, The present high demand for natural resources to meet infrastructural demands has created immense opportunities for the use of waste materials to green infrastructure construction, These waste materials play the roles of either supplementary cementitious materials (SCM) or alternative aggregates in green concrete and can be categorized as agricultural, industrial and municipal wastes Many waste materials can be used to utilize their pozzolanic properties in green, the waste materials are often activated through physical or chemical means or their combination ^[1-4]. One of the most pollutant materials is cement as, Approximately 3.6 billion tons of cement is produced globally every year. A conservative estimate for every 1 kg of cement produced gives a by-product of 0.9 kg of carbon dioxide, this equates to 3.24 billion tons of CO2 per year. From the combustion fuel used to heat the raw materials to sintering temperatures (1400–1600 C). The theoretical heat requirement for clinker-making is calculated to be about 1.75 \pm 0.1 MJ per kg^[5-7]. First step to reduce this source of pollution with reducing its amount in concrete, mortar and other construction purposes, using Supplementary cementations materials (SCMs) can achieve that were partially replacing by cement content, as Supplementary cementations materials can be used either as fillers or for their pozzolanic properties. They are composed of amorphous aluminosilicates, which react with excessive hydrated lime produced during cement hydration to form calcium aluminosilicate phase C-A-S-H^[8-10]. In Egypt most of the SCM is an industrial waste, which occure in Egypt with a large amount, as Solid Waste Management in Egypt (2013), 89.03 tons of solid waste, 6 million of which is an industrial waste. The number of industrial enterprises in Egypt is approximately 64,997 with industrial sectors in 2011 representing 37.6% of Egypt's GDP (Gross Domestic Product). This sector "impacts environmental degradation in Egypt to a substantial extent" with a steady increase in the amount of industrial waste produced in Egypt over the years. Initiatives to tackle the issue such as "Green Growth" [11],[12], as improper solid waste management leads to substantial negative environmental impacts, including health and safety problems such as diseases associated with different forms of pollution^[6].

II. RELATED WORK

An extensive research has been done all over the world in order to utilize and reuse the industry by-products in various construction applications. The addition of 10% silica fume has been found to increase the compressive strength of concrete cured at normal conditions ^[14], replacing cement by 5% marble dust could be a real energy and financial saving concept, in addition to saving part of the natural resources and alleviating the environmental ^[15], it can be replaced with sand to achieve adequate early compressive strength ^[16], when cement is replaced with marble powder up to10% weight a high strength concrete was achieved [17, 18]. impact imposed by the marble processing waste that the mix with nano-Silica from 1.5, 3, 5 or 7% or with nano-clay(by activated or and Silica Fume 10%, increase in inactivated phase) Compressive and flexure of concrete Strength and other properties^[19,20]. SCM and nano-materials not only fill microstructure pores but also act as Pozzolanic materials actively react with the CH from the hydration of the cement paste through the Pozzolanic reaction to produce more C-S-H. and more homogenous and stronger interfacial zone [21], [22], [23], and [24]

III. EXPERIMENTAL PROGRAM

III.I Materials and Mix Proportions:

Materials employed through this investigation, natural sand, cement, silica fume, fly ash, marble dust, air cooled slag, nano-silica, nano-clay(activated and inactivated), water.

Materials employed through this investigation, natural sand, cement, silica fume, fly ash, marble dust, air cooled slag, nano-silica, nano-clay(activated and inactivated), water. The cement used is Portland cement, (PC), (CEM I 42.5 - N). The employed fine aggregate in this investigation is natural siliceous sand from local quarry in Giza, it has a fineness modulus of 2.5. According to the grading shown in Figure (1), its particle size distribution lies within the range of fine grading zone according to the classification of the Egyptian code of practice for design of concrete structures (ECP 203-2007)[25], as it tested according to ASTM C136-96 standards [26]. Silica fume (SF) used in this study is a by-product of the production of silicon and ferrosilicon alloys. The used silica fume is locally produced and commercially available through metallurgical and construction chemical company. The chemical compositions are given in Table (1).

Table1. Chemica	l compositions of	the starting raw	materials
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Oxide	CEM 1 (%wt.)	SF (%wt.)	FA (%wt.)	FACS (%wt.)	MD (%wt.)	NC (%wt.)
CaO	63.3	0.24		41.2	43.5	16
SiO ₂	20.7	96.1	57.4	32.4	5.1	61.42
Al ₂ O ₃	4.63	1.31	9.6	12.3	0.5	20.89
Fe ₂ O ₃	3.63	0.57	6.1	0.6	0.7	1.06
MgO	1.63	0.23	3.1	5.5	14.6	0.22
SO ₃	3.25		5.91		0.04	0.17
K ₂ O	0.87	0.43	5.58		0.03	1.61
Na ₂ O	0.21	0.05	0.55		0.1	0.71
TiO ₂						0.70
P ₂ O ₅						0.12
KO ₂			1.077			
Ignition Loss	1.78	1.07			33.1	

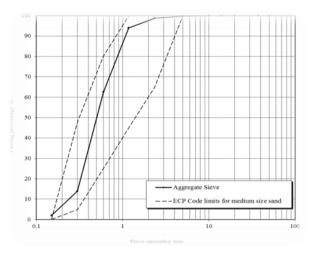


Fig. 1. Fine Aggregate Grading Curve according to ECP Code

Fly ash (FA) is a combustion residue (coal mineral impurities) in coal-burning electric power plants, which flies out with the flue gas stream and is collected by mechanical separators, electrostatic precipitators or bag filters. In this research a by-product material from the electric power station in Suez-Egypt was used. According to the chemical properties of fly-ash, introduced in table (1) the used fly ash is classified as class (F) in accordance with ASTM C618-12a limits [27].

FACS is a by-product from Iron and Steel Factory in Helwan-Egypt., its grading conforms to standard limits.

Nano silica used in this research was locally produced by twophase processing. Phase 1 by chemical preparation, and phase 2 by mechanical grading to get a fair dispersion for nano particles. The mean particle size is 38nm. The TEM image is introduced in fig.2.

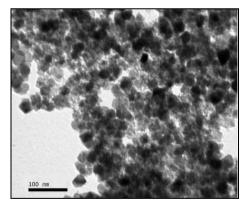


Fig.2. TEM of NS

The used nano clay type is supplied in the form of modified montmorillonite (hydrated sodium calcium aluminum silicate). It is a natural montmorillonite modified with an ammonium salt. The nano montmorillonite clay in its inactivated state is characterized by large length to thickness aspect ratio as shown in figure (3); it is especially favorable in matrix reinforcement. The mineral platelet thickness is only 1-10 nm, although its dimensions in length and width can be measured in hundreds of nanometers.

The nano-clay was thermally treated at 800°C for 2 hours to give active amorphous nano montmorillonite clay. figure (4) presents TEM of activated nano montmorillonite clay particles.

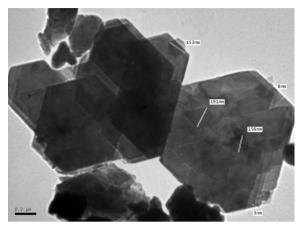


Fig. 3. TEM of as received NC



Fig. 4. TEM of activated NC

III.II Test Program and Specimens Fabrication

The by-product pozzolanic materials were grinded to be suitable for use as a cement replacement in mortar mixes. The mix designation of the investigated blended mortars is introduced in table (2).

		Na	no materials		By-product					
Mix	Mix C.C NS		ANC %	INC %	Туре	%	Sand %	W %	Curing	w/b
M1	100	0	0	0			275	48.5	W	0.485
M2	95	0	0	0	FA	5	275	48.5	W	0.485
M3	90	0	0	0	FA	10	275	48.5	W	0.485
M4	85	0	0	0	FA	15	275	48.5	W	0.485
M5	95	0	0	0	SF	5	275	48.5	W	0.485
M6	90	0	0	0	SF	10	275	48.5	W	0.485
M7	85	0	0	0	SF	15	275	48.5	W	0.485
M8	95	0	0	0	FACS	5	275	48.5	W	0.485
M9	90	0	0	0	FACS	10	275	48.5	W	0.485
M10	85	0	0	0	FACS	15	275	48.5	W	0.485
M11	80	0	0	0	FACS	20	275	48.5	W	0.485
M12	75	0	0	0	FACS	25	275	48.5	W	0.485
M16	96	0	0	0	FA	6	275	48.5	W	0.485
M17	96	0	0	0	FACS	6	275	48.5	W	0.485
M19	99	1	0	0			275	48.5	W	0.485
M20	97	3	0	0			275	48.5	W	0.485
M21	95	5	0	0			275	48.5	W	0.485
M22	93	7	0	0			275	48.5	W	0.485
M23	99	0	1	0			275	48.5	W	0.485
M24	97	0	3	0			275	48.5	W	0.485
M25	95	0	5	0			275	48.5	W	0.485
M26	93	0	7	0			275	48.5	W	0.485
M27	99	0	0	1			275	48.5	W	0.485
M28	97	0	0	3			275	48.5	W	0.485
M29	95	0	0	5			275	48.5	W	0.485
M30	93	0	0	7			275	48.5	W	0.485

IV. RESULTS

IV.I. Effect of Silica fume /Cement Percentage (SF/C %)

Figures (5, 6 & 7) show the effect of using silica fume as a cement replacement with constant cement content. The strength enhancement is a result of increasing the bond strength of cement paste aggregate interface by means of byproduct reaction and the filing effect of silica fume particles. The Figures show that the optimum percentage of silica fume was 15 % except 3 days compressive strength as the increase was 6.8%, 28.8% and 30.8% for 5%, 10% and 15% respectively, for 10 % silica fume, the results be too close to the optimum percentage. Therefore, it is clear that when silica fume added to cement mortar the optimum percentage can be used is 10% of cement content, it resulted in a significant change in the compressive strength of the mix. This is mainly due to the aggregate-paste bond improvement and enhanced microstructure. The addition of silica fume to mortar resulted in an improved bond between the hydrated cement matrix and sand in the mix, hence increasing strength. This improved bond is due to the conversion of the calcium hydroxide, which tends to form on the surface of aggregate particles, into calcium silicate hydrate due to the presence of reactive silica. The mix containing 15% silica fume as cement replacement showed maximum compressive strength with an increase of 30.8% at 28-day control mix without silica fume. The increase in strength for 10% silica fume was found 10%, 16.1% and 28.8% for the3, 7 and 28th days respectively compared to control one. Flow test results refer to a reduction in workability with increasing silica fume percentage until 10% then there is almost no reduction at 15% of silica fume replacement as shown in figure (7). Flexure strength had the same trend line for increasing strength with increasing silica fume percentage as flexure strength increase by 7.8, 14.5 and 20% at 3, 7, and 28-days respectively for 10% silica fume replacement and by 11.2, 22.2 and 26.8% at 3, 7, and 28-days respectively for 15% silica fume replacement as shown in figure (6).

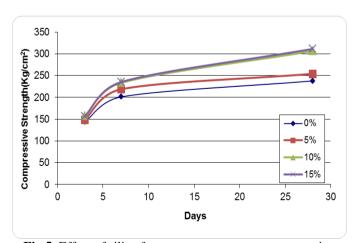


Fig.5. Effect of silica fume on cement mortar compressive strength

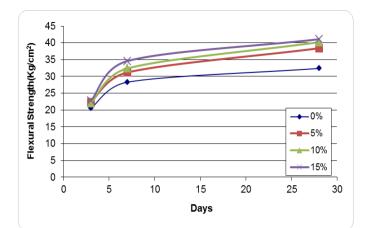


Fig.6. Effect of silica fume on cement mortar flexural strength

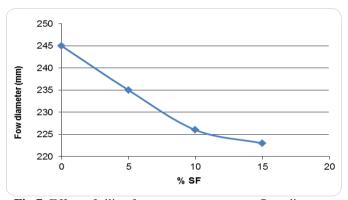


Fig.7. Effect of silica fume on cement mortar flow diameter

IV.II. Effect of Fly ash /Cement Percentage (FA/C %)

The compressive strength development of cement mortar containing various levels of fly ash presented in fig.8 as expected, at early age, the compressive strength of the mortar decreases with the increase amount of fly ash. The decrease in the 3 day strength of mortar mixes are proportionate to the fly ash content, where strength of the mortar with 5, 10, and 15% fly ash was lower by 4, 1.5 and 4.8% respectively. This behavior changed with curing time. At the age of 28 days, it is found that the cement mortar containing 5, 10 and 15% of fly ash exceeded the compressive strength of the plain mortar by 0.88, 6.9 and 2.2 % respectively as shown in figure (8). Figure (9) show the flexure strength for cement mortar containing 0. 5, 10 and 15% fly ash, results give indicate that flexure strength decrease with increase fly ash content at early age but its increase by increasing fly ash at 28-days till 10%, this results was compatible with compressive strength results. As shown in figure (10), Workability increase with increasing fly ash content in cement mortar. It is interesting to note that high volume fly ash often needs more than 7 days to acquire strength close to the plain concrete one. The continued increase in strength has been attributed to the by-product behavior of the ash, which endures to react with the cement to produce calcium silicate hydrate in presence of water.

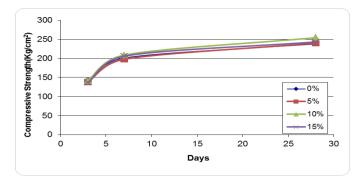


Fig.8. Effect of fly ash on cement mortar compressive strength

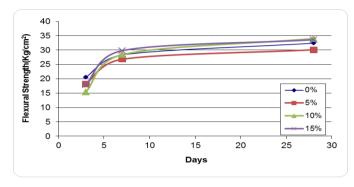


Fig.9. Effect of fly ash on cement mortar flexural strength

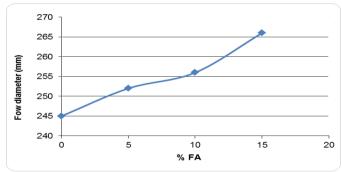


Fig.10. Effect of silica fume on cement mortar flow diameter

IV.III. Effect of Fine Air-Cooled Slag /Cement Percentage (FACS/C %)

Figures (11, 12 and 13) show the effect of using Fine Air Cooled Slag as a cement replacement with constant cement content. The figures show that the optimum percentage of Fine Air Cooled Slag was 15 % except 3 days compressive strength as the increase was 1.4 % and 1.55% for 7 and 28-days % respectively, for 5, 10, 20 and % Fine Air Cooled Slag, the results reduce compared to control and optimum mix. Therefore, it is clear that when Fine Air Cooled Slag added to cement mortar the optimum percentage can be used is 15% of cement content as shown in figure (10a), it resulted in a significant change in the compressive strength of the mix. For flexure strength there is no enhancement at early ages (3 and 7 days), even for the percentage 15% of Fine Air Cooled Slag results were too closed to control mix. Optimum

percentage achieved at 28 days by 15% of Fine Air Cooled Slag as a cement replacement, with 7.4% increasing more than control mix. Cement mortar mixes workability decrease with Fine Air Cooled Slag percentages increasing until 15%, then re-increase but still down the optimum and control mix.

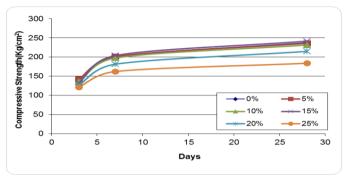


Fig.11. Effect of FACS on cement mortar compressive strength

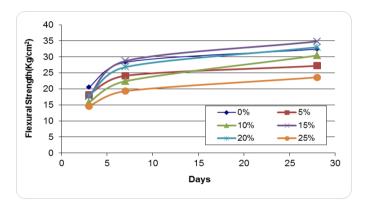


Fig.12. Effect of FACS on cement mortar flexural strength

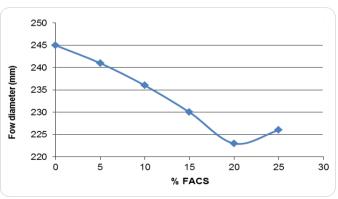


Fig.13. Effect of FACS on cement mortar flow diameter

IV.IV. Effect of Nano Silica /Cement Percentage (NS/C %)

Figure 14 shows the effect using nano silica as cement replacement on the compressive and flexure strength and flow diameter on cement mortar mixes. As shown in the figure (14), the compressive strength at age 3, 7 and 28-days increases with increasing of nano silica percentage. The strength increases till about 3% then decrease till 7%. For the tested mixes, the optimum mix were replacing cement by 3%

nano silica as compressive strength increase by 26.4, 34.4 and 38.5% at 3, 7 and 28-days respectively. For flexure strengthincreasing trend were almost the same to compressive strength with different value as optimum percentage also 3%, as flexure strength increase by 25.3, 30 and 33% at 3, 7 and 28-days, respectively as shown in figure (15). Workability clearly decreases with increasing nano silica percentage for all tested mixes as shown in figure (16).

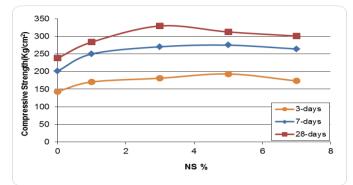


Fig.14. Effect of NS on cement mortar compressive strength

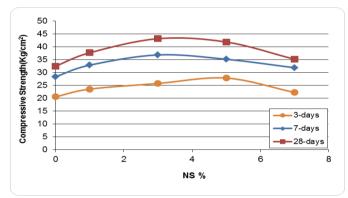


Fig.15. Effect of NS on cement mortar flexural strength

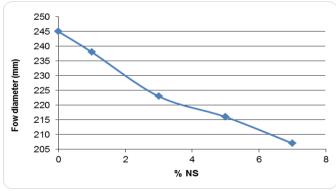


Fig.16. Effect of NS on cement mortar flow diameter

IV.IV. Effect of Activated Nano Clay /Cement (ANC/C %)

As shown in figure (17), the compressive strength at age 3, 7 and 28-days increases with increasing of activated nano clay percentage. The strength increases until about 3% then decrease till 7%. For the tested mixes, the optimum mix were replacing cement by 5% activated nano-clay as compressive strength increase by 20.4, 33.4 and 32.7 % at 3, 7 and 28-days respectively. For flexure strength-increasing trend were almost the same to compressive strength with different value as optimum percentage also 5%, as flexure strength increase by 37, 43.1 and 58.3 % at 3, 7 and 28-days, respectively as shown in figure (18). Workability clearly decreases with increasing nano silica percentage for all tested mixes as shown in figure (19).

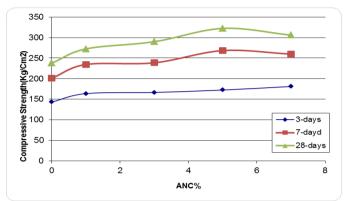


Fig.17. Effect of ANC on cement mortar compressive strength

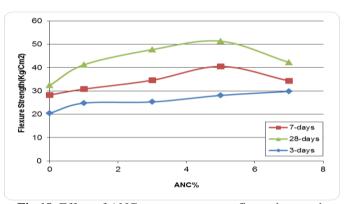


Fig.18. Effect of ANC on cement mortar flexural strength

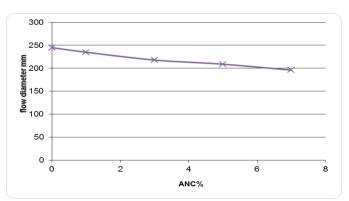


Fig.19. Effect of ANC on cement mortar flow diameter

IV.V. Microstructure characterization with Scanning Electron Microscope (SEM)

Figures (20a, b) show the SEM micro-graphs of the cement mortar samples with ordinary Portland cement and the mortar containing 3% NS as cement replacement. As it can be seen in

figure (20a), the SEM images show the microstructure characteristics of cement paste, few micro pores have been observed and less homogenity in micro and nano scale. Using 3% activated nano-clay (ANC) as cement replacement create homogenous C-S-H gel with good bonding characteristics, which explain the improvement in cement mortar samples strength more than all other materials used in this research as shown in figure (20b).

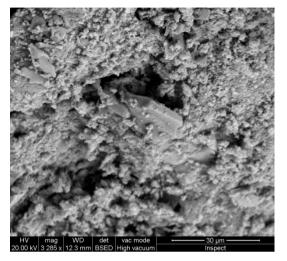


Fig.20a. SEM micrograph of control reference mix

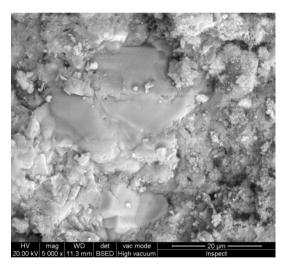


Fig.20b. SEM micrograph of 3% NS-modified mortar

VI. CONCLUSION

As the study aimed to produce green mortar, so more reduction in cement content mean more green product and less pollution and less cost, especially with more improvement in the product cement mortar properties such as compressive and flexural strength, that mean best results were using byproduct materials then nano-clay, finally nano-silica. Using byproduct materials not only aimed to reduce cement content, but also helping in reduce environmental pollution caused by such materials. Also the product green cement mortar becomes more durable, denser and sustainable for construction purposes.

Cement mortar mechanical properties such as compressive, flexure strength and workability had a noticed improved were using local byproduct and nano-materials as a partially cement replacement, such as, silica fume, fly ash, fine air-cooled slag, nano silica and activated nano-clay. Compressive strength is the main indicator for the other properties, as its improving directly refers to an enhancement for the other properties. Test results and optimum percentage briefly, as Compressive strength increase by 30.8, 6.9, 1.55, 38.5 and 32.7 %, more than control mix when use 15% SF, 10% FA, 15% FACS, 3% NS and 7% ANC, respectively. Flexure strength increase by 26.8, 4.9, 7.4, 33 and 58.3 %, more than control mix when use 15% SF, 10% FA, 15% FACS, 3% NS and 5% ANC, respectively. Workability for product green cement mortar decrease when using silica fume, fine air cooled slag nanosilica and nano-clay, but it increases when using fly ash and marble dust with selected optimum percentage.

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