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NANOMATERIALS IN TREATMENT AND CONSERVATION OF ARCHAEOLOGICAL BUILDINGS FAÇADES IN HISTORIC CAIRO AFFECTED BY AIR POLLUTION

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ABSTRACT

Islamic Cairo is a part of central Cairo noted for its historically important mosques and other Islamic monuments. Islamic Cairo was founded in (969 AD) as the royal enclosure for the Fatimid caliphs. Cairo contains the greatest concentration of Islamic monuments in the world, and its mosques, mausoleums, religious schools and baths were built between the seventh and nineteenth centuries. The air pollution in Cairo is a matter of serious concern. Archaeological buildings in Cairo suffer from different deterioration phenomena for example, black crust formation, chemical alterations, disintegration between surface mineral grains, pitting, cracks, missing parts, erosion, and white stains. Building materials which include limestone and marble in addition to salts and surface black crusts had been studied by polarizing microscope (PM), scanning electron microscope (SEM) and X-ray diffraction (XRD) to identify their components and their deterioration. Study for the effect of nano titanium dioxide and nano lime on stone samples was carried out. Results of stone samples treatment with nanomaterials were evaluated. Nano titanium dioxide gave a good effect in self-cleaning and nanolime (CaLoSiL IP25) gave the best result in consolidation of limestone and marble samples.

KEYWORDS:
Nanomaterials; Conservation; Limestone; Consolidation; Air pollution; Nanolime.

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المواد النانوية لعلاج وصيانة واجهات المباني الأثرية المتأثرة بالتلوث الجوي في القاهرة التاريخية

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الملخص

تشتهر القاهرة الإسلامية بمساجدها التاريخية ذات القيمة المعمارية والفنية الرفيعة. مدينة القاهرة تأسست عام (969م) كمقرًا للخلفاء الفاطميين، وتمثل القاهرة أكبر متحف مفتوح للعمارة الإسلامية بمختلف أنواعها تعكس تاريخ العمارة الإسلامية في مصر من القرن العاشر وحتى القرن التاسع عشر الميلادي. يشكل تلوث الهواء في القاهرة مصدر تلف بالغ، حيث تعاني المباني الأثرية في القاهرة من ظواهر تدهور مختلفة مثل تكوين القشرة السوداء، والتغيرات الكيميائية، والتفكك بين الحبيبات المعدنية السطحية، والتنقر، والشقوق، والأجزاء المفقودة، والتآكل. وقد تمت دراسة مواد البناء لبعض المباني الأثرية بمدينة القاهرة التي تشمل الحجر الجيري والرخام بالإضافة إلى الأملاح والقشور السوداء السطحية بواسطة الميكروسكوب المستقطب (PM) والميكروسكوب الإلكتروني الماسح (SEM)، وحيود الأشعة السينية (XRD) للتعرف على مكوناتها وعوامل تلفها وتدهورها. كذلك أجريت دراسة لتأثير نانو ثاني أكسيد التيتانيوم ونانو الجير على عينات الحجر، كما تم تقييم نتائج معالجة عينات الحجر بالمواد النانوية، وقد أظهرت النتائج أن نانو ثاني أكسيد التيتانيوم أعطى تأثيرًا جيدًا في التنظيف الذاتي وكذلك أعطي مركب نانو الجير (CaLoSiL IP25) أفضل نتيجة في تقوية الحجر الجيري والرخام.

الكلمات الدالة:

المواد النانوية؛ الصيانة؛ الحجر الجيري؛ التقوية؛ التلوث الجوي؛ النانو ليم.

INTRODUCTION

Islamic Cairo is a part of central Cairo noted for its historically important mosques and other Islamic monuments. It is overlooked by the Cairo Citadel. Islamic Cairo was founded in 969 AD as the royal enclosure for the Fatimid caliphs, while the actual economic and administrative capital was in nearby Fustat. Fustat was established by Arab military commander 'Amr ibn al-As' following the conquest of Egypt in 641 AD, and took over as the capital which previously was located in Alexandria. Al-Askar, located in what is now Old Cairo, was the capital of Egypt from 750 AD to 868 AD.[1] Ahmad Ibn Tulun established Al-Qatta'i as the new capital of Egypt, and remained the capital until 905 AD, when the Fustat once again became the capital. After Fustat was destroyed in 1168 AD /1169 AD to prevent its capture by the Crusaders, the administrative capital of Egypt moved to Cairo, where it has remained ever since.[2] It took four years for the General Jawhar Al Sikilli (the Sicilian) to build Cairo and for the Fatimid Calif Al Muizz to leave his old Mahdia in Tunisia and settle in the new Capital of Fatimids in Egypt. Fustat became a regional center of Islam during the Umayyad period. Later, during the Fatimid era, Al-Qahira (Cairo) was officially founded in 969 AD as an imperial capital just to the north of Fustat. [3] Over the centuries, Cairo grew to absorb other local cities such as Fustat, but the year 969 AD is considered the "founding year" of the modern city. In 1250 AD, the slave soldiers or Mamluks seized Egypt and ruled from their capital at Cairo until 1517 AD, when they were defeated by the Ottomans.[4] By the 16th century, Cairo had high-rise apartment buildings where the two lower floors were for commercial and storage purposes and the multiple stories above them were rented out to tenants. Napoleon's French army briefly occupied Egypt from 1798 AD to 1801 AD, after which an Albanian officer in the Ottoman army named Muhammad Ali Pasha made Cairo the capital of an independent empire that lasted from 1805 AD to 1882 AD. The city then came under British control until Egypt was granted its independence in 1922 AD. Cairo is a world heritage city. It contains possibly the finest collection of monuments in the Islamic world. It contains some of the best surviving monuments of the medieval period in the Islamic world.[5]. The wealth, prosperity, and power of Cairo are reflected in the grand architecture of the monuments that are crowded together into the Fatimid city and just beyond, Fig. (1). [6] Cairo's Islamic monuments are part of an uninterrupted tradition that spans over a thousand years of building activity. No other Islamic city can equal Cairo's spectacular heritage, nor trace its historical and architectural development with such clarity. [7] Cairo contains the greatest concentration of Islamic monuments in the world, and its mosques, mausoleums, religious schools, baths, and caravanserais, built by prominent patrons between the seventh and nineteenth centuries, are among the finest in existence [8], fig. (2) Shows some of Islamic archaeological buildings in Cairo. The air pollution in Cairo is a matter of serious concern. Greater Cairo's volatile aromatic hydrocarbon levels are higher than many other similar cities. Air quality measurements in Cairo have also been recording dangerous levels of lead, carbon dioxide, sulphur dioxide, and suspended particulate matter concentrations due to decades of

[1] Creswell, *The Muslim Architecture of Egypt*, 112.
[2] Beattie, *Cairo: A Cultural History*.
[3] Butler, *The Arab Conquest of Egypt*.
[4] Behrens-Abouseif, *Islamic Architecture in Cairo* ; Daly, and Petry, *The Cambridge History of Egypt*.
[5] Christopher and Boxberger, "*Ottoman Cairo*".
[6] Mortada, *Traditional Islamic principles of built environment*, p. viii.
[7] Williams, *Islamic Monuments in Cairo*.
[8] Anoniou, *Historic Cairo - A Walk through the Islamic City*.

unregulated vehicle emissions, urban industrial operations, and chaff and trash burning. There are over 4,500,000 cars on the streets of Cairo, 60% of which are over 10 years old, and therefore lack modern emission cutting features like catalytic converters. Cairo has a very poor dispersion factor because of lack of rain and its layout of tall buildings and narrow streets, which create a bowl effect. Cairo also has many unregistered lead and copper smelters which heavily pollute the city. The results of this have been a permanent haze over the city with particulate matter in the air reaching over three times normal levels.[9] Pollutants are deposited on the surface of stone from the air. Where the surface of the stone is totally dry, the stone is discolored as the deposits increase. Where the surface of the stone is moist, the pollutants are converted to acids that eat away the surface of the stone by dissolving the binder in the stone causing the stone particles or grains to separate and erode away easily.[10] Carbon dioxide, Nitric oxides, and Sulphur oxides product mineral acids in humid conditions. They dissolve the calcium and magnesium carbonates in limestone, marble, lime mortars, and plasters in archaeological buildings. Archaeological buildings in Cairo suffer from different deterioration phenomena for example, black crust formation, chemical alterations, disintegration between surface mineral grains, pitting, cracks, missing parts, erosion, and white stains.[11] Stone consolidants should ideally, be physically and chemically compatible with the materials requiring consolidation. Nano-lime has been used as a method of consolidating limestone, marble and lime plasters because it offers theoretical advantages over traditional materials such as limewater and lime grouts.[12] Preliminary investigations to determine its performance characteristics prior to its specification and subsequent use on stone were undertaken by Hirst Conservation in 2010. Although these tests were limited to only a few materials, results were encouraging and highlighted some of the product's advantages and disadvantages. The results clearly show that rates of penetration vary significantly according to the type of material, its porosity and other factors.[13] Nano-lime dispersed in alcohol can work well as a consolidant if used in the correct manner, allowing time for maximum penetration, precipitation and carbonation of the nano-lime. This may take days or even weeks for each saturation.[14] The development of self-cleaning surface treatments could be very promising in order to preserve original aesthetic aspect of surfaces and to decrease the deposition of pollutants, reducing soiling and the onset of degradation processes on stone surfaces.[15] Self-cleaning surfaces are available in nature, such as lotus plant leaves and the exoskeleton of some insects. This natural self-cleaning property depends on superhydrophobicity of this kind of surfaces, and is ascribed to the interdependence between surface roughness, reduced particle adhesion and water repellence of the surfaces themselves: the so-called “lotus effect”.[16] These features can be reproduced artificially, but superhydrophobic man-made surfaces could degrade during a long outdoor exposure and they could not have compatibility with some kind of substrate. Superhydrophobicity is not the only way to prevent soiling processes obtaining easy-to-clean surfaces. Self-cleaning

[9] Watt, et al. “Soiling by atmospheric aerosols,” 1285–1289.
[10] Aksu, Horvath, et al. “Measurements of the deposition velocity of particulate matter to building surfaces,” 675–676.
[11] Davidson, Tang, Finger, Etyemezian and Sherwood SI, “Soiling patterns,” 560–565.
[12] Giorgi, Ambrosi, Toccafondi and Baglioni. “Nanoparticles for Cultural Heritage Conservation,” 9374-9382.
[13] Ziegenbalg, Brümmer, and. Pianski. “Nano-Lime - a New Material for the Consolidation and Conservation of Historic Mortars.” pp. 1301-1309.
[14] Daniele, and Taglieri, “Nanolime suspensions applied on natural lithotypes,” 102-6.
[15] Benedix, Dehn, Quaas, Orgass, “Application of titanium dioxide pho-tocatalysis to create self-cleaning building materials,” 157–68.
[16] Barthlott, Neinhuis, “Purity of the sacred lotus, or escape from contamination in biological surfaces,” 1–8.

effect is also obtained by the use of superhydrophilic and photocatalytic materials.[17] The superhydrophilic property prevents the soil from adhering to the treated substrate through the formation of an uniform water film over the solid surface, while photocatalysis can decompose most of the organic and inorganic pollutants in contact with coated surface under ultraviolet (UV) irradiation, causing a de-pollution effect too.[18] The synergy of hydrophilic and photocatalytic effects could preserve aesthetical properties and improve surface maintenance, reducing degrading processes due to soiling phenomena. Titanium dioxide (TiO_2) is one of the most important and common photocatalysts because of its outstanding efficiency (even under weak solar irradiation), inexpensiveness, compatibility with a large number of materials and good stability; moreover UV light induces superhydrophilicity of TiO_2, so it can be applied to solid surfaces to obtain self-cleaning effect.[19] In the field of building materials, titanium dioxide is one of the most used and efficient photocatalysts for realizing self-cleaning, de-polluting and self-sterilizing surfaces.[20] This paper aims to study deterioration and decay of building materials in archaeological buildings in Cairo because of air pollution, discussion and explanation of deterioration phenomena which forming in archaeological building in Cairo according to air pollution and discussion of different methods and materials of treatment, restoration and conservation of building material in archaeological buildings from deterioration phenomena related to air pollution. On the other hand, study using of nanoparticles in treatment and conservation of limestone and marble of archaeological buildings façades in historic Cairo affected by air pollution.

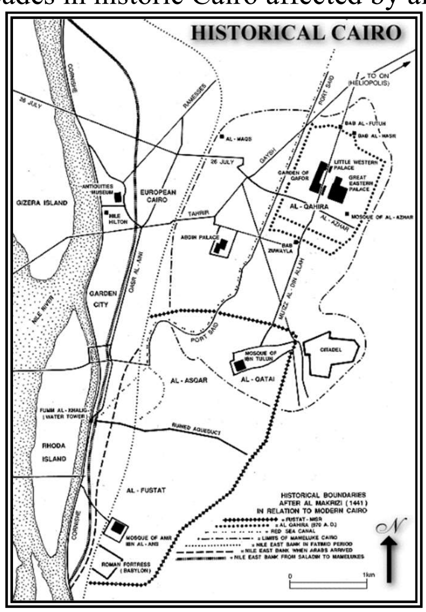

Fig. (1) shows a map of historical Cairo.
http://www.touregypt.net/Map08.htm.

SOURCES OF AIR POLLUTION IN CAIRO

Air pollution plays a major role in the deterioration of building materials used in historic buildings. Industrial facilities such as factories and plants emit toxic gases into the atmosphere. Another major source of toxic emissions in Egypt is the widespread open-air

[17] Fujishima, Rao, and Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobio. C 1 (2000) 1–21.
[18] Luvidi et al. “Application of TiO_2 based coatings on stone surfaces of interest in the field of cultural heritage,” 495–500.
[19] Kolen’ko et al. “Photocatalytic properties of titania powders,” 51–8.
[20] J. Chen, C. Poon, “Photocatalytic construction and building materials: from fundamentals,” 1899–1906.

burning of trash and waste. Waste landfills also give off methane, which, although not toxic, is highly flammable and can react in the air with other pollutants to become explosive.[21] There are numerous sources to air pollution in Egypt, as in other countries. However, the formation and levels of dust, small particles and soot are more characteristic in Egypt than presently found in industrialized countries. Some of the sources for these pollutants, such as industries, open-air waste burning and transportation, were also well known problems in most countries only 10 to 20 years ago. Another important source for particulate matter is the wind blown dust from the arid areas. Suspended dust (measured as PM10 and TSP) can be seen to be a major air pollution problem in Egypt. PM10 concentrations can exceed daily average concentrations during 98% of the measurement period. On the other hand it seems that the natural background of PM10 in Egypt may be close to or around the air quality limit value. These levels can be found also in areas where local anthropogenic sources do not impact the measurements. Further measurements may be used in the future to quantify the relative importance of the different sources relative to a background level that varies dependent upon the area characteristics. In addition to particles, also SO_2 in urban areas and in industrial areas, as well as NO_2 and CO in the streets may exceed the Air Quality Limit value. Major industrial pollutants include sulphur oxides, nitrogen oxides, carbon monoxide and carbon dioxide. [22] For instance, Cairo is surrounded by various industrial sites. Thirty Kilometers to the south of Cairo is Helwan, where different factories produce iron, steel, coke, chemicals, automobiles, and cement. To the north of Cairo are Shubra Al – Khayma, Musturud, and Abu Zabal. In this area factories produce dyes, textiles, glass, ceramics, and chemical products. All of these factories emit different pollutants (gaseous, liquid, solid), which are carried by the dominant winds (north and northeast, and west or south, southwest) down to Cairo, many of the historic buildings are located. Every day Cairo receives a high dose of pollutants composed of 52 percent carbon monoxide (CO), 14 percent sulphur dioxide (SO_2), 21 percent hydrocarbons, 10 percent dust, solid materials, and 2 percent (NOx) nitrogen oxides, The dust particles from the Muqattam hills to the east of Cairo was 27 gm / m2 / month in 1962. This increased to more than 60 gm / m2 / month in 1988, with a particularly high amount in the summer when the aerosols of dust in the air were more than 500 gm / m2 / month[23] [15]. Many Egyptians rely upon extremely old vehicles for transportation. These inefficient vehicles cause the carbon present in fuel to ineffectively react with oxygen during combustion, producing carbon monoxide or condensing to form particles of soot. The hydrocarbons do not combust completely and are released as gaseous hydrocarbons or absorbed by particles, increasing the particulate mass in the air. The speed at which pollutants disperse in the air is determined by meteorological conditions such as wind, air temperature and rain. Egypt and Cairo, particularly, have a very poor dispersion factor due to lack of rain and the layout of streets and buildings, which are not conducive to air flow.[24] Emissions that arise from the combustion of solid fossil fuels are of prime concern. Coal and oil both contain sulphur in varying amounts, and both therefore produce sulphur dioxide when burnt. There are a number of nitrogen oxides (NOx), but the one of principal interest as an air pollutant likely to have adverse effects on human health and soiling properties is nitrogen dioxide (NO_2). Nitrogen compounds are also contributors to the wet and dry deposition of acidic compounds on vegetation and buildings. Particulate

[21] Air Pollution Levels Measured in Egypt Exceeds Air Quality Limit Values. (2002), EEAA/EIMP, Ministry of state for Environmental Affairs, Egyptian Environmental Affairs Agency.
[22] Hopkins; N. 2003"The Environmentalist: Living with Pollution in Egypt".
[23] Abo El-Ela, A., The Impact of Environmental pollution on the Mosque of Al-Azhar," pp. 99-114.
[24] Del Monte M, Sabbioni C and Vittori O, "Airborne carbon particles and marble. deterioration," 2253–2257.

matter is a term that represents a wide range of chemically and physically diverse substances that can be described by size, formation mechanism, origin, chemical composition, atmospheric behavior and method of measurement. The concentration of particles in the atmosphere varies across space and time and as a function of the source of the particles and the transformations that occur to them as they age and travel. Particles less than 10 mm in diameter (PM10) are often measured that include both fine and coarse dust particles.[25]

MATERIALS AND METHODS

Limestone and marble samples of original stones and crusts were collected from different deteriorated parts of archaeological buildings, according to the decay and the damage levels fig. (3) as follows: - Limestone samples from El- Ghouri Mosque, El–Mahmoudya Mosque, Taghri Bardi Mosque and Lagen El – Sayfi Mosque. - Marble samples from Qaitbay Sabil, Taghri Bardi Mosque and Azbak El- Yusufi Mosque.

Fig. (2) shows some of Islamic Archaeological buildings in Cairo: (A) El- Sultan Hassan Madrassa (1362 AD / 764 AH) and El – Refae Mosque. (B) El-Mosabeh Mosque(1792 AD / 1192 AH). (C) El- Ghouri Mosque in El – Sayeda Aisha Square (1504 AD / 909 AH). (D) El – Mahmoudya Mosque (1568 AD / 975 AH). (E) Qaitbay Sabil (1479 AD / 884 AH). (F) Taghri Bardi Mosque (1439 AD / 843 AH). (G) Azbak El- Yusufi Mosque. (H) Singer and Slar Mosque (1303 AD / 703 AH). (I) Lagen El – Sayfi Mosque (1296 AD / 696 AH).

[25] Del Monte, Sabbioni and Vittori, 2253–2257.

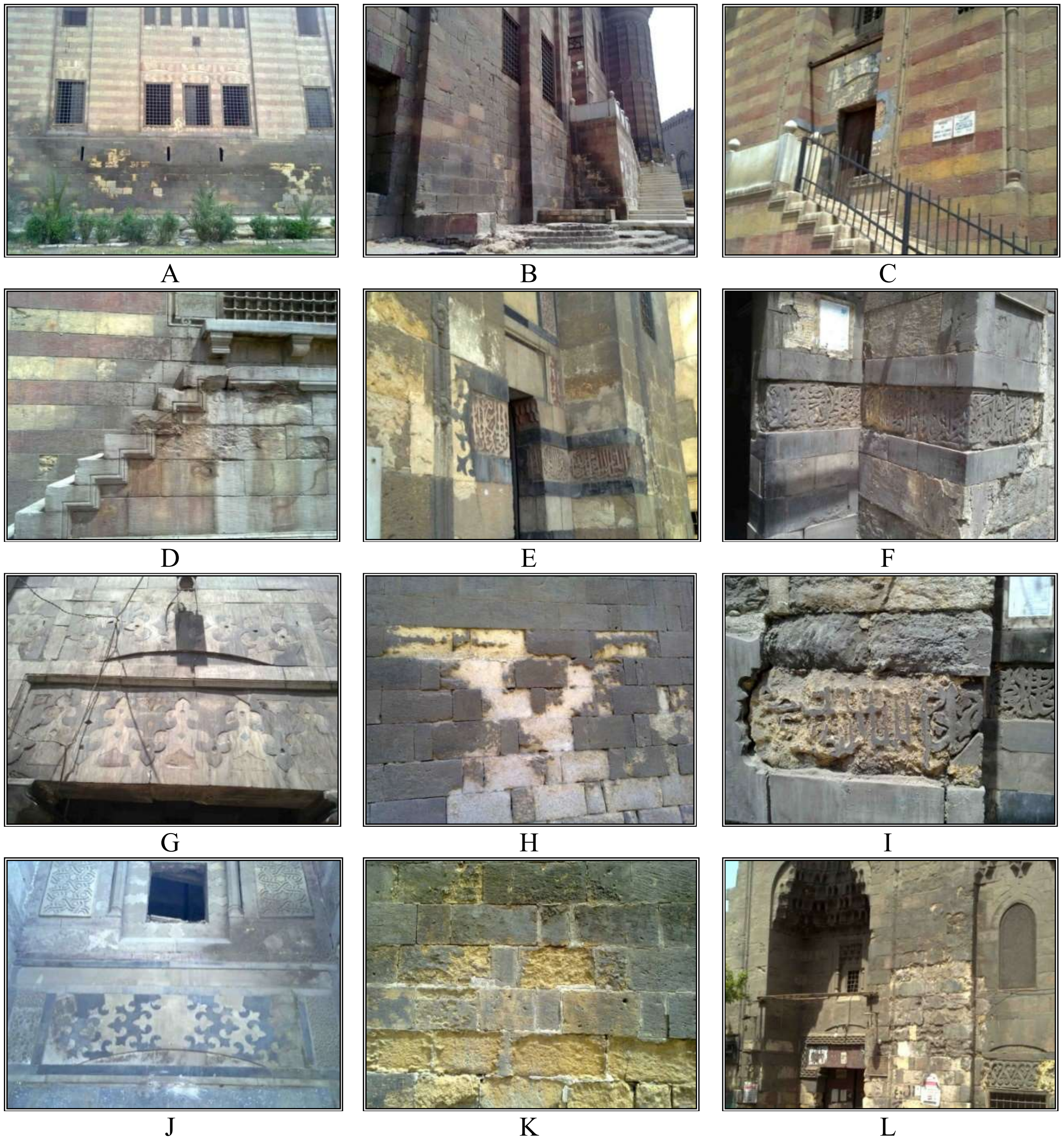

Fig.(3) Shows some details of Islamic Archaeological buildings, (A) , (B) , (G) El – Mahmoudya Mosque (1568 AD / 975 AH). (C) , (D) Qanibay Al – Ramah Mosque (1503 AD / 908 AH). (E) Qaitbay Sabil (1479 AD / 884 AH) (F) , (H) , (I) , (L) Taghri Bardi Mosque (1439 AD / 843 AH). (J) Lagen El – Sayfi Mosque (1296 AD / 696 AH). (K) Azbak El- Yusufi Mosque (1494 AD / 900 AH).

Analytical study have been carried to selected samples by polarizing microscope [PLM], scanning electron microscope [SEM], energy dispersive X-ray analysis [EDX], X-ray diffraction (XRD) and FTIR analysis. The x-ray diffraction analysis of samples was carried out using philips x-ray diffractometer. The operating conditions were: Generator applied on a Cu kα radiation (1.5418 A°) with Ni filter, 40 KV, 20 mA° target tube. Scavenging velocity 2° per minute and chart velocity 5 mm per minute were applied in Bulk sample powder. Fragments of crusts collected were prepared for observation using scanning electron microscope (SEM), operated at accelerating voltage of 30 kV. Infrared spectra were recorded employing a Nicolet Nexus 870 FTIR spectrometer. A small amount of samples were mixed with KBr and pressed into pellets, then scanned from 4000 to 400 cm^{-1}. CaLoSiL E25 and CaLoSiL IP25 used to consolidate the limestone and marble samples, fig. (9). CaLoSiL contains nanoparticles of lime hydrate [$Ca(OH)_2$] suspended in different alcohols. Typical concentrations are between 5 and 50 g/L. The average particle size is 150 nm. The extremely fine size of the synthetic nano-lime results from its preparation, which is based on chemical synthesis. Ethanol, iso-propanol or n-propanol serves as solvents. Due to the low particle size stable sols are formed that means the solids do not sediment for a long time. CaLoSiL is a ready-to-use stone consolidant. An aqueous sol of titania (TiO_2 content: 1% by weight) was prepared through sol-gel technique starting from tetrapropylorthotitanate (TPOT) as titania precursor that was added dropwise to a bihydrate oxalic acid water solution. The amount of titania deposited for square meter is 0.40 g for three layer deposition.

RESULTS AND DISCUSSION

Limestone samples were examined by polarizing microscope (PM) and, it is found that: Samples consist mainly of fine-grained calcite besides presence of iron oxides, quartz, clay minerals and fossils include nummulite fossils these components increase the rate of stone decay[26], fig. (4 , A-F). On the other hand the thin section of fragments taken from marble objects shows that the major mineral is calcite, The crystals appeared in mosaic texture, The crystals have irregular faces and highly variable grain size, the cleavage planes of the calcite crystals and the presence of rare and very little amount of opaque minerals[27] fig. (4, G-I). When the limestone samples were examined by [SEM], it is found disintegration between calcite crystals and the stone lost the binding materials between grains by the effect of salts crystallization fig. (5, A-D). Examination of marble samples by [SEM] shows that, erosion of calcite crystals, presence of salts because of chemical reaction with climatic conditions, alteration of calcite into gypsum because of air pollution effect, voids and disintegration between grains by crystallization of salts stresses and lose of binding material[28] fig. (5, E-F). XRD data fig. (6) (A-D) shows that, the examined limestone samples consist of calcite $CaCO_3$, Card No. (5-0586) in addition to gypsum $CaSO_4.2H_2O$ Card No. (6-0046), quartz SiO_2 ,Card No. (5-0490), halite Card No.(5-0628) and dolomite Card No.(11-078) . XRD data of the marble samples shows that, they consist of calcite $CaCO_3$, Card No. (5-0586) in addition to Dolomite Ca,Mg(CO3)2, Card No. (11-078), and Halite, NaCl Card No. (5-0628) fig (5-a). and anhydrite, Card No (6-0226) fig (5-c). The surface of the marble is covered by a crust of hydrated calcium sulphate (gypsum) related to reaction with air pollution in presence of moisture. Gypsum crusts are the most common type of growth found on building surfaces. Gypsum is calcium sulphate dihydrate, with the chemical formula $CaSO_4.2H_2O$. Gypsum crusts are formed on calcareous stones following SO_2 deposition to the surface in the presence of moisture, followed by the dissolution of calcite and the precipitation of gypsum. The black color of gypsum crusts is the result of the accumulation of particulate matter within the crust[29]. When the water evaporates from soluble salts as chlorides, it leaves behind concentrations of salt solutions which crystallize on the stone surfaces and between mineral grains of stone, this process cause disintegration and deterioration of stone[30]. Energy dispersive X-ray analysis (EDX) of limestone samples shows that it consists of calcium element (Ca), sulphur element (S), silicon element (Si) and sodium element (Na) in addition to traces from other elements. The relative enrichment of Si, Al and Fe might be derived from the deposition of wind-borne articles since the

[26] Khallaf, "Role of Investigation and Analytical Methods in study of Archaeological Stone."
[27] Khallaf, "Analysis and Preservation of Marble in Archaeological Buildings.".
[28] Khallaf, "Degradation and Conservation of Marble Floors in Archaeological Buildings."
[29] Khallaf, "Environmental Deterioration and Conservation Studies of Building Materials of Qaitbay Citadel.".
[30] Saiz-Jimenez, *Air pollution and cultural heritage*..

archeological stone buildings in Cairo are near a road with much traffic[31] fig. (2). Rich-S is originated from SO_2 emitted by anthropogenic sources like combustion of fuels, automobile emissions, foundries and smelters. EDX data shows high content of calcium related to calcite mineral, silicon and aluminum due to clay minerals, silicon due to quartz mineral, iron related to iron oxides, sodium and chlorine due to presence of halite salt fig (7) (A-D). Rich-Ti-Mn is associated with industrial and urban emissions. The fly-ash particles play an active role in the damage processes affecting stone, since the content of transition metal oxides contribute to the catalytic oxidation of atmospheric gaseous SO_2 and to the sulphation of calcium carbonate. XRD, SEM, EDX results show that black crusts are essentially composed by gypsum crystals, fly ashes and soot, including some limestone and marble materials. Fly ashes usually are rich in Si and Al with higher or lower amounts of K, Fe, Ca, Ti and Cl. Combustion of fuel and natural gas in car engines and house heating originates carbon rich soot about one hundred times smaller than fly ashes.[32]. The term ‘‘atmospheric particulate material’’ refers to all airborne particles, so it is by definition non-specific. It includes material from such diverse sources as, for example, vehicle emissions, the resuspension of surface dusts and soils and chemical reactions between vapours and gases in the atmosphere, which result in the formation of secondary particles[33]. Therefore emission inventories of PM relate to primary sources of PM only (not secondary sources)[34]. The principal types of primary particulate material are Petrol and diesel vehicles, the latter being the source of most black smoke[35]. Controlled emissions from chimney stacks and fugitive emissions. These are diverse and mostly uncontrolled and include the resuspension of soil by wind and mechanical disturbance [36]. The resuspension of surface dust from roads and urban surfaces by wind, vehicle movements and other local air disturbance[37]. Emissions from activities such as quarrying, road and building construction, and the loading and unloading of dusty materials[38]. Secondary particles are those arising when two gases or vapours react to form a substance that condenses onto a nucleation particle,[39]. The main sources of secondary particles are the atmospheric oxidation of sulphur dioxide to sulphuric acid and the oxidation of nitrogen dioxide to nitric acid; the sulphuric acid is present in air as droplets, the nitric acid as a vapour,[40]. Hydrochloric acid vapour (arising mainly from refuse incineration and coal combustion) is also present in the atmosphere, and both this and nitric acid vapour react reversibly with ammonia to form ammonium salts,[41]. Sulphuric acid reacts irreversibly in two stages to form either ammonium hydrogen sulphate or ammonium sulphate. These ammonium salts are formed continuously as sulphur dioxide and nitrogen dioxide are oxidised, and ammonia becomes available for neutralization,[42]. FTIR spectra of a limestone sample fig. (8) shows that the characteristic absorption peaks of $CaCO_3$ is at 1798, 1424, 874, 711 cm−1, the characteristic absorption peaks of, CO_3-apatite [$(Ca_5(PO_4)_3)2CO_3$] is at 565, 604, 1040 cm−1 and the characteristic absorption peaks of gypsum is at 672, 1623,

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31 Parker, The *destructive effect of air pollution on materials*, 3–15.
32 Watt, “Automated Characterisation of Individual Carbonaceous Fly Ash Particles,” 309–327.
33 Pesava P, et al. “Dry deposition of particles to building surfaces and soiling,” 25–35.
34 Pio CA et al., “Atmospheric aerosol and soiling of external surfaces in an urban environment,” 1979–1989.
35 Brimblecombe, *The effects of air pollution on the built environment*.
36 Hamilton and Mansfield, “Airborne particulate elemental carbon: its sources,” 715–723.
37 Hinds, *Aerosol Technology: properties, behaviour and measurements of airborne particles*.
38 Tidblad, Mikhailov and Kucera, *Acid deposition effects on materials in subtropical and tropical climates*.
39 Kucera and Tidblad, “Comparison of environmental parameters and their effects on atmospheric corrosion.”.
40 Cole, “Mechanisms of atmospheric corrosion in tropical environments.”
41 Maeda, Moriocka, et al., “Materials damage caused by acidic air pollution in East Asia,” 141–150.
42 Beloin and Haynie, “Soiling of building materials,” 393–403.

3408 cm^{-1}.The results of infrared spectroscopy are also confirmed by XRD analysis which provides information on the crystalline components. The limestone contains Calcite and quartz, and gypsum. In consideration of the high average relative humidity and rainwater in the environmental conditions in Cairo, the most probable process of crust formation on stone substrate is the absorption of sulphur dioxide in rainwater, liquid atmospheric aerosols or moist film supported on a stone surface,[43] where it is oxidized to form a sulphuric acid solution that dissolves the calcium carbonate by gypsum formation. Kaolinite has been identified on a stone flake collected from a washed-out surface [44]. Its presence can be related to calcite dissolution, which is strongly enhanced by its exposition to rainwater and winds [45]. The deposition of wind-born soil dust on the surface may also be a source of kaolinite.[46] The mineralogical, textural and physicochemical differences of the examined crusts suggest that it is unlikely that they have the same origin or the same pattern of development[47]. In Cairo, high relative humidity, frequent fogs, sulphur, nitrogen pollutants, carbonaceous and deposition of airborne particles either on exposed or sheltered areas of Cairo archaeological buildings[48]. In consequence of these processes, these deterioration products grow on sheltered areas leading to thick encrustations, which are washed-out on surfaces exposed to rainwater[49]. On the unsheltered surfaces, newly formed soluble salts, washed-out by water and percolated through the bedding planes of the stone substrate, create a network of parallel and deep fissures, which increase the stone susceptibility to further deterioration[50]. On the other hand archaeological buildings in Cairo suffer from soiling, fig. (3). Soiling is a visual effect resulting from the darkening of exposed surfaces following the deposition and accumulation of atmospheric particles[51]. Deposition, removal and accumulation processes are numerous and complex,[52] depending on the physical and chemical properties of the particles, the nature of the surface, the local meteorology and the pathways followed by rainwater after it hits the building surface[53]. As a result of these complex interactions, there can be substantial variations in the level of soiling observed on building surfaces. It is one of the effects of air[54]. Limestone and marble samples have been treated with CaLoSiL E25 and CaLoSiL IP25 for consolidation. Results which have been obtained from physical and mechanical properties measurements as well as SEM examinations fig. (10,11) shows that, CaLoSiL IP 25 gave the best result in consolidation processes. It increased the mechanical properties and improved the physical properties, tables (1, 2). Treatment of stone with CaLoSiL results in the formation of solid calcium hydroxide after evaporation of the alcohol. That converts into calcium carbonate in a way similar to traditional lime mortars by reaction with atmospheric carbon dioxide. All alcohols evaporate without any residues. Chemicals or residues deteriorating stone or mortar are not formed. The calcium hydroxide particles formed from CaLoSiL after evaporation of the alcohol cover the surface of treated cracks,

[43] Hamilton and Mansfield, "The soiling of materials in the ambient atmosphere," 3291–3296.
[44] Lanting, "Black smoke and soiling in aerosols: research, risk assessment and control strategies."
[45] Mansfield and Hamilton, "The soiling of materials: models and measurements."
[46] Parker, "The destructive effect of air pollution on materials," 3–15.
[47] Gauri, and Holdren, "Pollutant effects on stone monuments," 386–390.
[48] Delalieux, Cardell, and Todorov, "Environmental conditions controlling the chemical weathering," 43–54.
[49] Moropoulou, Bisbikou and Torfs, "Origin and growth of weathering crusts on ancient marbles," 967–982.
[50] Maravelaki-Kalaitzaki, "Black crusts and patinas on Pentelic marble from the Parthenon," 187–198.
[51] Vazquez-Calvo, Buergo, and Fort, "Characterization of patinas by means of microscopic," 1119–1132.
[52] Brimblecombe and Grossi, "Aesthetic thresholds and blackening of stone buildings," 175–198. Fig. 4.15 Variation of soiling with PM10 concentration (white painted steel) 124.
[53] Mack, and Grimmer, *Assessing Cleaning and Water-Repellent Treatments for Historic Masonry Buildings*.
[54] Khallaf, "Interfacial Characteristics of Polymeric Coatings for Archaeological Stones Conservation."

pores or joints. Dense films of calcium hydroxide films are formed, depending on the number of treatment cycles and the concentration of the used sols.[55] Typical particles sizes are in the range of few hundred nano-metres. Their detection by means of standard optical microscopy may be difficult, the use of SEM is recommended. Calcium carbonate formation by reaction with atmospheric carbon dioxide requires the presence of humidity. Depending on the conditions and the amount of calcium hydroxide brought into stone, mortar or plaster carbonations takes place within few days and weeks.[56] In some cases, after treatment by spraying of water aerosols on the treated materials may be used to accelerate the carbonation process. Results also show that nano TiO_2 protected the surfaces of limestone and marble samples. It was clear from the measurements specially, static contact angle measurements, fig. (12), table (3). Limestone samples have been treated with nano titanium dioxide for protection from environmental pollution. Environmental pollution arising from industrial implants and urban factors is constantly increasing, causing aesthetical and durability concerns to urban structures exposed to the atmosphere. Nanometric titanium dioxide has become a promising photocatalytic material owing to its ability to catalyze the complete degradation of many organic contaminants and environmental toxins.[57]

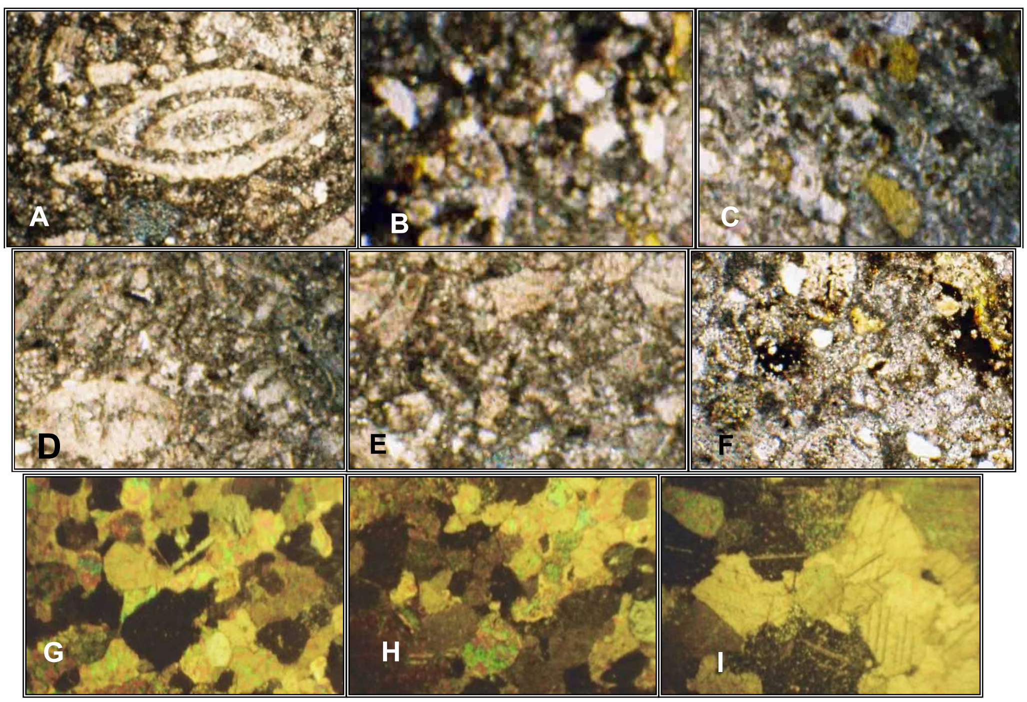

Fig. (4) (A-F) Thin section photomicrographs showing iron oxides, clay minerals, fossil and grains of quartz in a mass ground of fine- grained calcite. 60X (C.N). (G-I) shows that it is a mosaic texture; the calcite crystals have irregular faces and cleavage planes ,120X (C.N).

This work deals with building materials in order to improve the quality of urban surfaces, with particular regard to cultural heritage. TiO_2-containing photoactive materials represent an appealing way to create self-cleaning surfaces, thus limiting maintenance costs, and to promote the degradation of polluting agents.[58]

[55] Dei, and Salvadori, "Nanotechnology in Cultural Heritage Conservation," 110–115.
[56] Drdácký, Slížková and Ziegenbalg, "A Nano Approach to Consolidation of Degraded Historic." 13-22.
[57] Zielinska, Grzechulska, Grzmil, Morawski, "Photocatalytic degradation of reactive Black 5," L1–L7.
[58] Giorgi, Ambrosi, Toccafondi and Baglioni. "Nanoparticles for Cultural Heritage Conservation," 9374-9382.

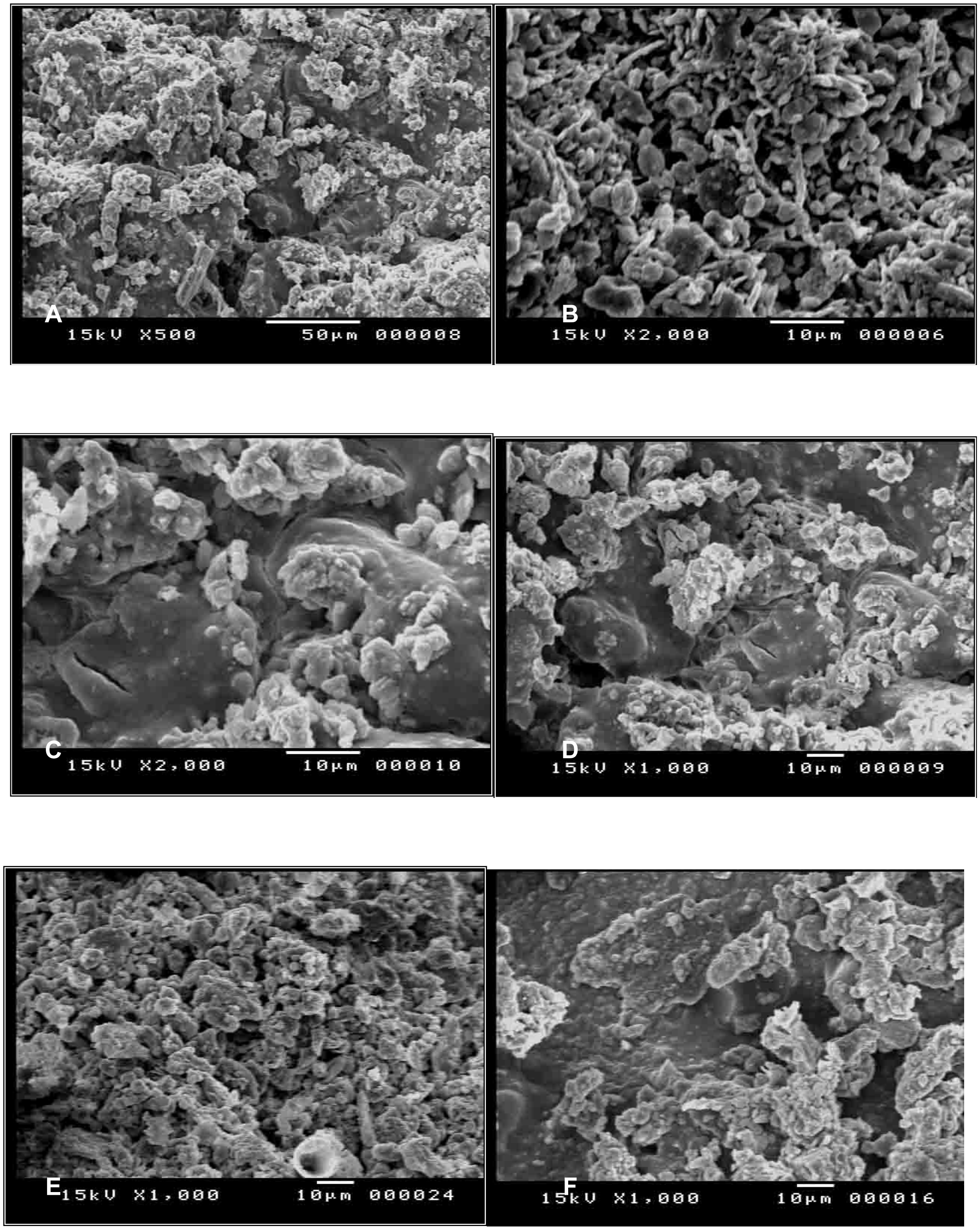

Fig. (5) (A-D) SEM photomicrographs of limestone samples showing the collapse of internal structure , salts crystallization between grains of limestone ornaments.(E-F) photomicrographs of Marble samples showing voids due to lose of binding material erosion, discoloration, a coat of Carbon (C-D), chipping, fly ashes in a black crust and particles from the combustion of fuel oil and coal, containing a quantity of Carbon, Iron, Manganese and Sulphur.

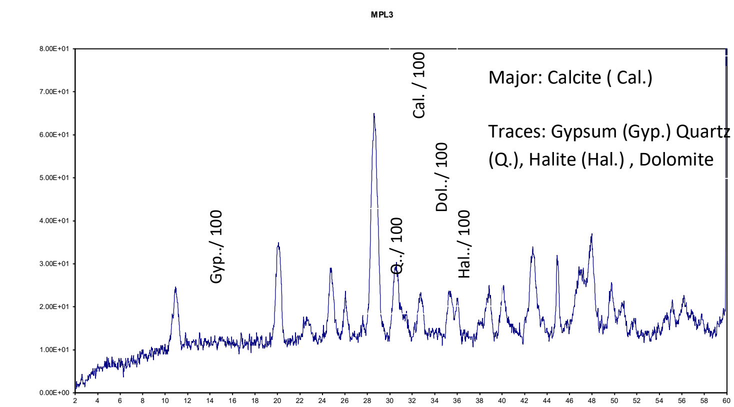

Fig. (6-A) shows XRD patterns of Limestone sample from El- Ghouri Mosque.

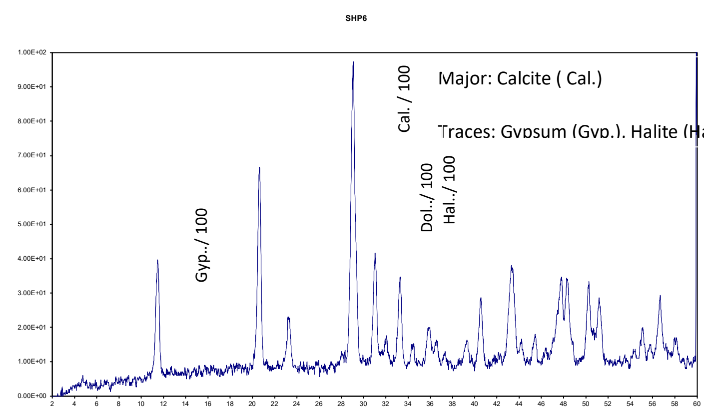

Fig. (6-B) shows XRD patterns of Limestone sample from El – Mahmoudya Mosque.

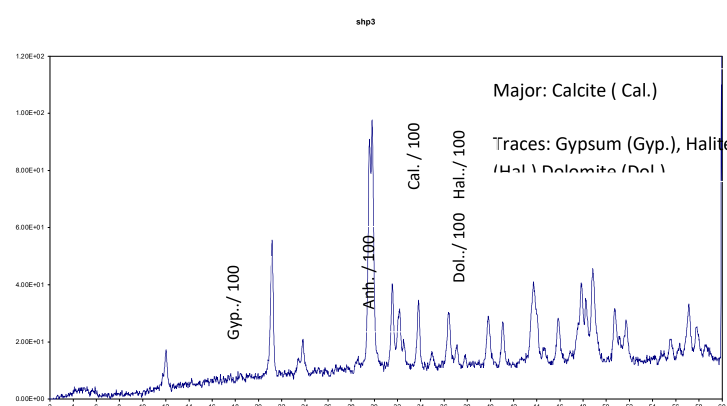

Fig. (6-C) shows XRD patterns of Marble sample from Taghri Bardi Mosque.

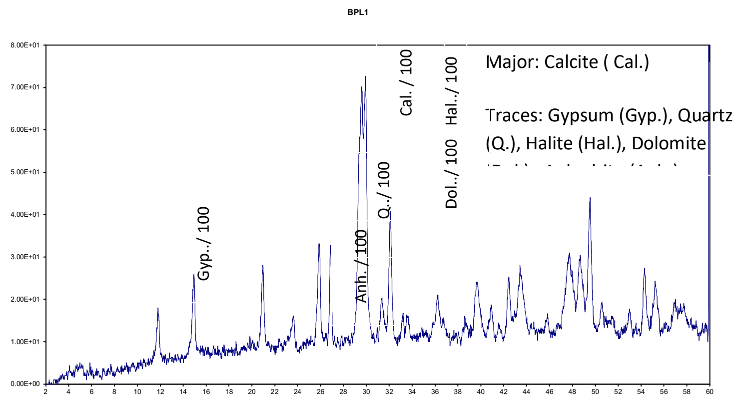

Fig. (6-D) shows XRD patterns of Marble sample from Qaitbay Sabil.

Atomic%	Weight%	Element
69.16	45.02	O K
1.98	2.17	Al K
5.40	6.17	Si K
2.27	2.96	S K
0.62	0.99	K K
1.69	2.75	Ca K
9.20	17.92	Ti K
0.45	1.00	Mn K
9.25	21.01	Fe K
	100.0	Total

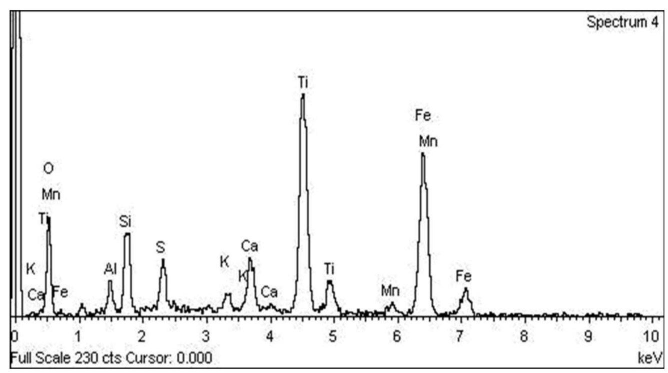

Fig. (7-A) shows EDX patterns of limestone sample from El- Ghouri Mosque.

Atomic%	Weight%	Element
49.75	36.59	C K
38.35	37.58	O K
0.46	0.65	Na K
0.21	0.41	P K
5.26	10.32	S K
0.52	1.14	Cl K
0.63	1.50	K K
4.81	11.81	Ca K
	100.0	Total

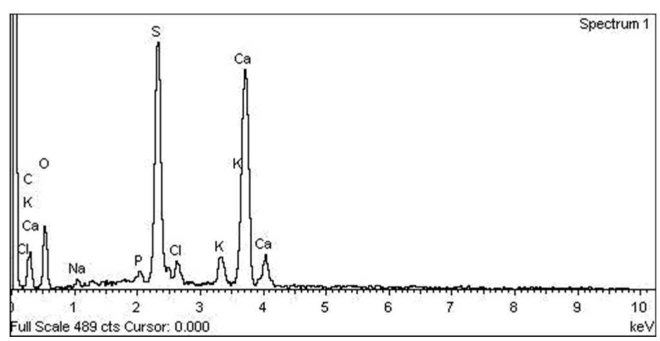

Fig. (7-B) shows EDX patterns of limestone sample from El – Mahmoudya Mosque.

Atomic%	Weight%	Element
75.34	58.45	O K
1.35	1.51	Na K
0.72	0.85	Mg K
0.63	0.83	Al K
2.10	2.85	Si K
0.14	0.21	P K
7.27	11.30	S K
1.32	2.27	Cl K
1.35	2.57	K K
9.57	18.60	Ca K
0.21	0.56	Fe K
	100.0	Total

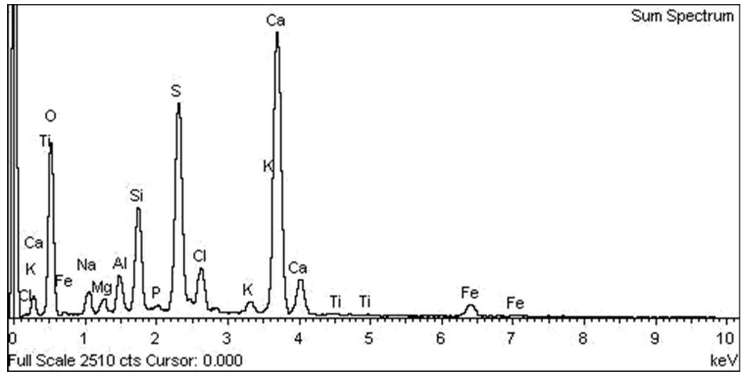

Fig. (7-C) shows EDX patterns of Marble sample from Taghri Bardi Mosque.

tomic%	eight%	lement
2.72	1.40	K
5.38	5.40	K
86	21	a K
17	33	K
99	79	K
22	49	l K
47	14	K
18	0.25	a K
	00.0	otal

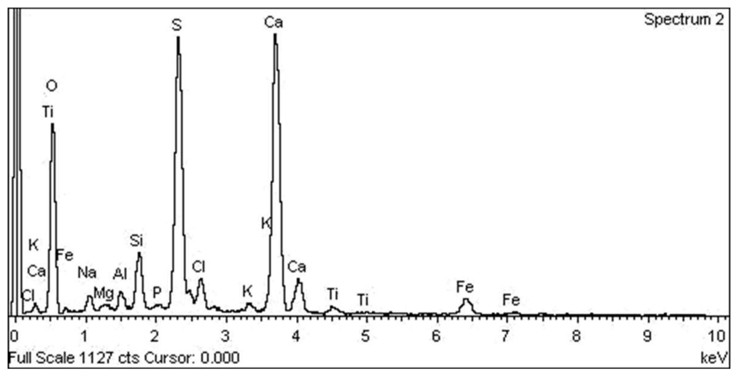

Fig. (7-D) shows EDX patterns of Marble sample from Qaitbay Sabil.

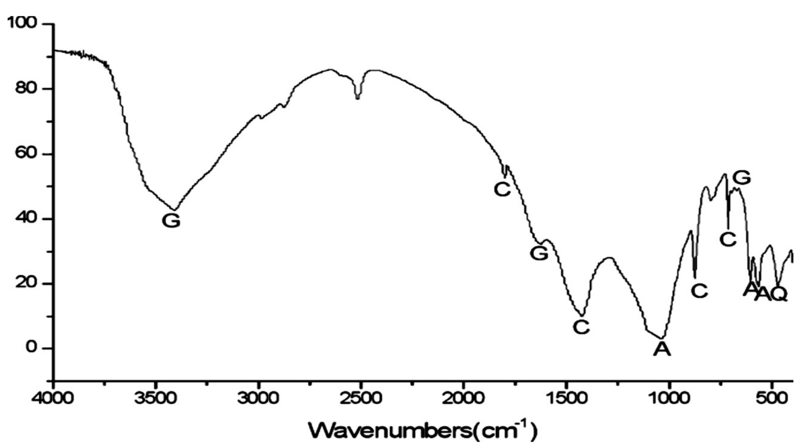

fig. (8) FTIR spectra of limestone sample from El – Mahmoudya Mosque C, calcite (1798, 1424, 874, 711 cm−1); G, gypsum (672, 1623, 3408 cm−1); A, apatite (565, 604, 1040 cm−1); Q, quartz (469 cm−1).

Fig. (9) shows Limestone samples , CaLoSiL IP25 and CaLoSiL E25.

Table (1) shows the physical and mechanical properties of limestone samples before, after treatment.

Limestone Property	Calosil IP 25		Calosil E 25
	Before	After	After
Bulk Density gr/cm^3	2.1	2.4	2.2
Water Absorption%	6.2	4.7	5.2
Porosity %	14.6	8.9	10.8
Comprasive Strength Kgm/cm^2	174.5	271.6	257.4
Tensile Strength Kgm/cm^2	24.3	35.3	30.6

Table (2) shows the physical and mechanical properties of marble samples before, after treatment .

Marble Property	Calosil IP 25		Calosil E 25
	Before	After	After
Bulk Density gr/cm^3	7.9	9.2	8.8
Water Absorption%	2.1	1.8	1.9
Porosity %	3.2	2.3	2.6
Comprasive Strength Kgm/cm^2	382.3	463.7	418.9
Tensile Strength Kgm/cm^2	81.1	39.4	37.3

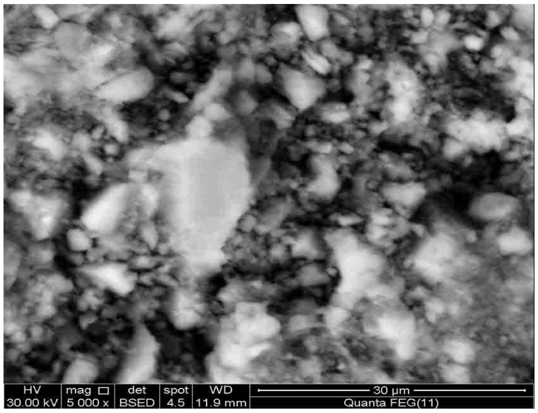

Fig (10) shows SEM photomicrographs of marble sample after treatment by CaLoSiL IP25 and nano TiO_2 with best penetration depth.

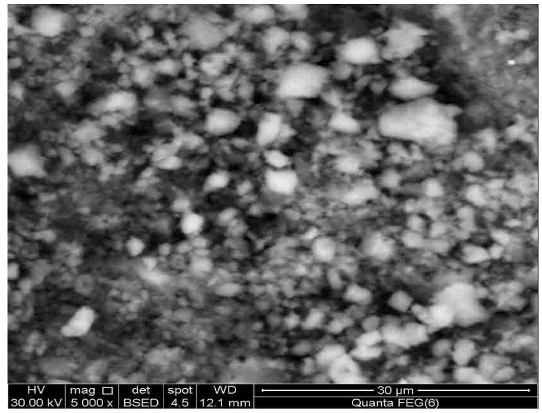

Fig (11) shows SEM photomicrographs of limestone sample after treatment by CaLoSiL E25 and nano TiO_2 with best coating.

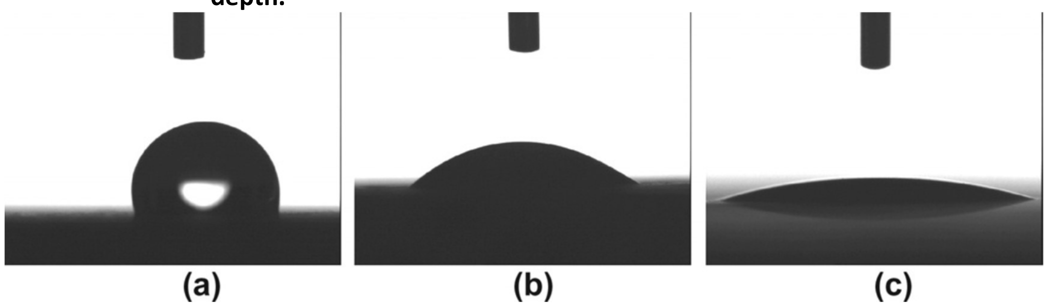

Fig. (12) Water drop on untreated surface (a), Marble (b), and Limestone (c).

Table (3) shows static contact angle average values (±standard deviation) as a function of titania content.

CA $_{initial}$		Marble	Limestone
	71.6 ± 10.9	18.4 ± 6.3	124 ± 2.3

CONCLUSION

The danger to archaeological buildings from air pollution comes from two main sources – gases that increase the corrosivity of the atmosphere and black particles that dirty light-colored surfaces. Acid rain comes from oxides of sulphur and nitrogen, largely products of domestic and industrial fuel burning and related to two strong acids: sulphuric acid and nitric acid. Sulphur dioxide (SO_2) and nitrogen oxides (NOx) released from power stations and other sources form acids where the weather is wet, which fall to the Earth as precipitation and damage both heritage materials and human health. In dry areas, the acid chemicals may become incorporated into dust or smoke, which can deposit on buildings and also cause corrosion when later wetted. Atmospheric chemistry is, of course, far more complex than this and a variety of reactions occur that may form secondary pollutants that also attack materials. Particulate matter is much more complicated because it is a mixture rather than a single substance – it includes dust, soot and other tiny bits of solid materials produced by many sources, including burning of diesel fuel by trucks and buses, incineration of garbage, construction, industrial processes and domestic use of fireplaces and woodstoves. Particulate pollution can cause increased corrosion by involvement in a number of chemical reactions and, often more importantly, it is the source of the black matter that makes buildings dirty. The influence of heavily polluted atmosphere in the urban environment results in different weathering patterns, mainly in the form of crusts. It might be assumed that the analytical results of Polarizing Microscope, XRD, SEM, EDX and IR. Alone are not sufficient to clarify and interpret the growth mechanisms of crusts. However, they do provide valuable information about changes in compositions of crusts and original rock, and the relationship between crusts composition and air pollution. The compositions of the crusts collected from areas on the archaeological stone buildings with different decay patterns show that the deterioration is mainly due to the atmospheric pollutants and its extent is strongly dependent on the surface exposition to the environment. According to the obtained results, an appropriate conservation plan will be developed, that includes the steps of cleaning and consolidation, in order to identify the most suitable materials and methodologies to remove the deterioration crusts avoiding the loss of original substrate and ensuring an increased cohesion to deteriorated stone. Finally, nanolime (CaLoSIL IP25) is a successful consolidant for protection and conservation limestone and marble in archaeological buildings from weathering and air pollution and nano TiO_2 is a good agent for limestone and marble self-cleaning.

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