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# Air pollution, black crusts and Cairo monuments: a review

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***Abstract* – Recently, the degradation phenomena affecting built cultural heritage and relative to environmental pollution increased considerably. The monuments in Historic Cairo are particularly exposed to these processes and their conservation is seriously threatened. The present review considers the studies about degradation products such as black crusts and salt crystallization affecting the building materials of selected monuments. The minero-petrographical and geochemical characterization will allow establishing the connections between them and the environmental pollution, such as the atmospheric one in terms of heavy metals and carbonaceous fraction. All specimens underwent a multi-methodological approach, the results highlighted that black crusts and salt crystallization represent the most common degradation products affecting all the monumental sites. Additionally the correlation between the composition of black crusts and the main pollutant sources in Cairo such as vehicular traffic and industrial activities was clarified.**

## Introduction

Cairo is considered one of the most polluted cities in the world because of the emissions constituted of particulate matter and high levels mostly of sulphur dioxide and lead. They are related to the strongly congested vehicular traffic and industrial activities, considering the high density of population reaching 13107/km$^2$. Moreover, the hot arid climate and the consequent lack of rain promote the accumulation of pollutants in the air. Studies on atmospheric aerosols emissions and road dust report the great contribution of heavy metals from industrial and urban sites in Greater Cairo Area [1]. In this context, the formation of degradation products such as black crusts in building stones is highly favored especially on carbonate substrates such limestones. They are one of the main building materials in the historical monuments of the Mediterranean area, but equally they are affected by degradation phenomena such as the above mentioned black crusts and salt crystallization [2-4]. Black crusts form through sulphating processes of the stone surface where calcium carbonate ($CaCO_3$), which is the main constituent of limestone, is transformed into gypsum $CaSO_4{*}2H_2O$ [5]. Metals and metal oxides, present in the atmosphere, catalyse the sulphating reaction. Moreover particulate matter, which contains mainly amorphous carbon and several heavy metals, can be embedded into the gypsum, providing its characteristic black colour [6]. Thus, black crusts produce aesthetic damages and hardening, they become difficult to remove from the substrate worsening the state of conservation of the monuments. Whereas, the salt crystallization can produces efflorescence and sub-efflorescence phenomena able to damage seriously the inner structure of the stone substrate. The research is a part of an Executive program for scientific cooperation between the Italian Republic and the Arab Republic of Egypt, entitled “Characterization of black crusts formed on historical buildings under different levels of ambient air pollution in Cairo and Venice”.

## I. MATERIALS AND METHODS

Limestones coming from the local quarries of Mokattam and Helwan areas have been used for the construction of monuments in Cairo since Pharaonic times until today [2]. In this regards, 23 samples of black crust and substrate were taken from the following monuments in Historic Cairo at various heights (ranged between 0.20 m and 2.50 m) and from vertical surface: the outer walls of Salah El-Din citadel, the tower of Bab Al Azab, the Manial Palace, Magra El-Oyoun wall, the Mosque of the Sultan Faraj ibn Barquq, the Qaitbay Mosque, the Silahdar Mosque and the tomb of Qansuh Al-Ghuri. The samples underwent polarized optical microscopy (POM) to obtain minero-petrographic information; X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) to identify mineralogical species in the black crust; Ion chromatography (IC) to quantify the main anions and cations present in the black crust; Electron Probe Micro Analyser coupled with energy dispersive X-ray spectrometry (EPMA-EDS) to observe the micro-morphology and analyse the composition in terms of major chemical elements; laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to obtain chemical analyses of the black crusts, as well as of the substrates, in terms of trace elements; TGA (Thermo-Gravimetric Analysis) instrument to quantify the carbonaceous fraction in terms of OC (Organic Carbon), EC (Elemental Carbon) and CC (Carbonatic Carbon).

## II. RISULTS AND DISCUSSION

### *A. POM Analysis*

Limestones are classified mostly such as biomicrite, followed by intramicrite and biosparite [7]. The substrates inside, show a fair state of conservation with some cases of internal fracturing or secondary porosity, for example, relative to dissolution of the bioclasts. The black crusts show an average thickness of 100 µm and reaching in some cases 400-500 µm. Microcrystals of gypsum, quartz, opaque minerals and carbonaceous particles have been identified. The contact layer/substrate is commonly linear and sharp (Fig.1).

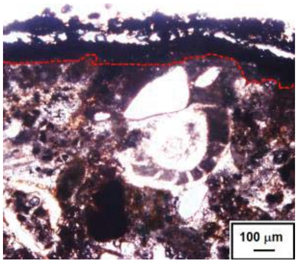

*Fig. 1. Microphotographs in OM showing biomicrite substrate and black crust associated. The red lines highlight the contact between the two components. (Plane Polarized Light view ) [8].*

### *B. IC Analysis*

The IC analysis on the black crusts determined the main cationic ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and $NH_4^+$) and anionic ($NO_3^-$, $SO_4^{2-}$, $Cl^-$) species were determined for each sample revealed an obvious predominance of calcium and sulphate ions because main components of gypsum. Anyway beyond sulphates, also chloride and nitrates are abundant. Generally the main sources are the infiltration of groundwater, sewage, lack of infrastructure system and the consequent water rising for capillary action; the sea spray. In the case of sulphates, atmospheric pollution provides the most relevant contribution to their crystallization processes thanks to the high concentration of sulphur dioxide available [8]. Chlorides based salts, in particular Halite (NaCl), are the most common ones, because Egyptian limestone contain them naturally, and a great amount comes from sea spray Chlorides are very dangerous, because they can produce intense sub efflorescence and consequently micro-cracks and the destruction of the pore structure in the stone [2].The origin of nitrates is closely relative to the nitrogen pollutants present in the atmosphere and linked for example to the domestic and industrial fuel burnings.

### *C. FT-IR Analysis*

The main components detected in all the crusts are gypsum, oxalate and calcite, typical black crusts compounds. The presence of oxalate, according to the scientific literature, could be related to restoration works carried out in the past or to the presence of biological activity [8-10]. Calcite derives from the substrate.

### *D. XRD Analysis*

The analysis on the crusts revealed the presence of gypsum, calcite and secondarily quartz as the main mineralogical species. Quartz and calcite come from the limestone substrate, while gypsum from is the main constituent of the crusts [3,6]. Among the other mineralogical phases, plagioclase, K-feldspar, hematite, clay minerals and halite were identified in subordinate amount.

### *E. EPMA-EDS Analysis*

EPMA-EDS morphological analysis revealed the irregular morphology of the crusts, their good adherence to the substrate. Acicular crystal of gypsum and sub-spherical carbonaceous particles were recognized. The chemical analysis suggested how CaO is the predominant component, followed by $SiO_2$, $SO_3$, secondly by ClO, $Al_2O_3$, $Na_2O$, $K_2O$, FeO and lastly by MgO, $P_2O_5$ and $TiO_2$.

### *F. LA-ICP-MS Analysis*

Trace elements concentrations were determined by LA-ICP-MS spot analysis on the black crusts and underlying substrates of all the examined samples. Pb, Ba, V, Cr, Co, Zn and As have relatively high concentrations, indicating an accumulation of atmospheric pollutants on the gypsum crusts, regardless of the sampling location. All these elements can be introduced in the urban environment by a wide range of different anthropogenic processes, mainly mining, smelting, industrial manufacturing, metal processing, etc. [11], domestic and residential activities (heating, vehicles, transport) but also by natural processes as erosion of rocks. The Enrichment factor calculation is useful to determine the anthropogenic origin of chemical elements, in particular of heavy metals, metalloids and Rare Earths Elements (hereafter REE). In this way, it will be possible to define the relation between pollution sources and degradation state of stone materials. The chemical procedure was followed by normalizing the chemical composition of trace elements in black crusts with respect to those of calcareous substrates on which they grew. This calculation is carried out by comparing the concentrations of the trace elements with those of the conservative element (Sc) by following the formula EF = (M/N)sample/(M/N)substrate, which is the ratio between the concentrations of the metal (M) and those of the normalizer (N), both for the sample and for substrate samples [12]. The crusts analysed are enriched in Zn, As, Pb, Co, Mo, REE (L-REE, light and H-REE, heavy) and Sn, Ba, Pb and HREE, respectively. Some heavy metal and metalloids concentrations (V, Cr, Co, Ni, Zn, As, Cd and Pb, Mn and Cu) in the studied black crusts, suggest their provenance from the road dust [1]. Instead the highest values of As and Cd are related to their use in the industrial sector, i.e. man-made emissions from metal smelters, mining activities, combustion processes (coal and oil) and refuse incineration.

### *G. TGA Analysis and Carbonaceous fraction*

The analysis of carbonaceous material is of great interest for the study of black crusts [13-16]. The EC fraction has a graphitic structure and represents a primary pollutant, directly emitted during the combustion processes related to e.g. traffic and biomass burning. The OC fraction is composed of different classes of compounds (e.g. hydrocarbons, oxygenated) and may have a primary or secondary origin (formed from gaseous precursors such as VOC). The carbonaceous components are involved in some heterogeneous chemical reactions that occur in the atmosphere, acting with $SO_2$, $NO_2$, $O_3$ and other gaseous components [17]; they are also responsible for some degradation processes, accelerating the corrosion phenomena of metals or the formation of black crusts [18-20]. In addition to EC and OC, the carbonaceous fraction of the black crusts also includes the CC (carbonatic carbon), coming from the stone substrate and oxalates (Ox), whose origin may depend on different factors as previously described in the FT-IR/ATR study. The quantification of the carbonaceous species, are required particularly in urban areas in order to investigate atmospheric deposition processes on building surfaces, to get information on the possible particulate matter (PM) sources and to suggest mitigation measurements to fulfil a better conservation of the stone surfaces. In this regard, it is important to consider the climate factor: the Mediterranean region, and thus Cairo area, is characterized by an intense photochemistry during summer which brings to high concentration in the aerosol PM of secondary organic substances. Thermogravimetric analysis provided data as percentages by weight (wt.%) of TC (Total Carbon= OC+EC), OC (Organic Carbon); EC (Elemental Carbon); Ox (Oxalate), Gy (Gypsum). In general, all the crust samples show higher EC values (wt. %) than OC. According to [21] the polluting sources contributing to the OC fraction into the air in Cairo are mainly represented by industry, residential, energy production and incinerators, while EC is mainly emitted from mobile sources (diesel traffic) and combustion processes (e.g. domestic heating or industrial activities) [22]. Data collected suggest that the concentration of EC increases when the sampling height of the crusts decreases. This confirms that the main source of this pollutant could be vehicle traffic which is responsible for the emission of particles which mainly affects surfaces at lower heights in direct contact with the road. The OC value on all the analysed samples varies from a minimum of 0.36 to a maximum of 1.88, while that of EC varies from a minimum of 0.99 to a maximum of 5.95. A further confirmation of our statement arises, comparing the OC/EC ratio with that performed on the carbonaceous aerosols [23]. Generally, relatively low values equal to or less than 1 are attributable to primary emissions and combustion of fossil fuels [24], while ratios greater than 1 usually indicate different polluting emissions. The ratios obtained for Cairo samples vary from minimum value of 0.23 and maximum 0.75 indicate that the polluting sources that have likely affected the accumulation of the carbonaceous fraction in the black crusts of Cairo are primary sources including vehicular road traffic.

In fact, it has been highlighted that for urban sites in Europe [25], where vehicular emissions are the dominant source of pollution, the values obtained from the OC/EC ratios fall in the range 0.3-0.7, suggesting a low contribution of secondary OC.

## III. CONCLUSIONS

The work highlighted how the built cultural heritage in Historic Cairo is affected by different and harmful degradation phenomena closely linked, firstly, to the intense environmental pollution. In particular, the results show the strong correlation between the atmosphere composition and the degradation processes affecting stone materials used. In this regard, the research underlines the importance of the reduction of emissions in atmosphere as first step for an efficient conservation strategy of the monuments in Historic Cairo then followed by suitable restoration interventions based, for example, on appropriate cleaning procedures, consolidating and protective products.

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