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Influence of Air Pollution and Humidity on Limestone Materials Degradation in Historical Buildings Located in Cities Under Tropical Coastal Climates

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Abstract Climatic changes and the increased air pollution intensify the atmospheric degradation of stone, affecting the aspect and integrity of valuable historical buildings constructed using limestone and located in tropical coastal sites. This paper analyzes limestone degradation process due to air pollution and humidity in tropical humid conditions in historical buildings located in the cities of Havana, Cuba and San Francisco de Campeche, Mexico. Havana shows higher pollution level than San Francisco de Campeche, which presents pollution levels as a consequence of a multipollutant situation along with the presence of airborne salinity. Temperature and humidity data were recorded from the walls of historical buildings in the city of Havana: the Minor Basilica and the convent of San Francisco. Changes in dry/wet cycles due to the absence of direct sun radiation as well as a high level of SO_2 allow the formation of a black crust (mainly composed of gypsum) in the lower part of the surface of the facade of the Basilica Minor in Havana; however, crusts formed in historical buildings located in San Francisco de Campeche City are mainly composed of calcium carbonate, indicating the importance of natural degradation mechanisms mainly due to dissolution in water. In the last case, the influence of water plays an important role in the development of biodegradation, which induces the formation of calcium oxalates. Caves and cracks were found in the walls of military buildings caused by water infiltration. The influence of air contamination, humidity, and construction materials determine the type of degradation that historical buildings undergo.

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1 Introduction

Since ancient times, stone is known as the most durable building material, remaining as a common base construction material today. However, climate changes and the augmented air pollution may cause a substantial increase in stone degradation.

Limestone consists almost entirely of calcite, the most stable polymorph of calcium carbonate ($CaCO_3$). Also, a small content of aragonite is usually found in limestone (Graedel 2000). Carbonate stone tends to be highly porous, usually about 15–20% (or even as much as 45%) for most limestone. Water and chemical species dissolved in water have straightforward access to the porous system of the limestone affecting their durability. It is very probable that stone structures undergo degradation due to the co-associated action of physical, chemical, and biological agents. Three well-defined physico-chemical degradation mechanisms have been established (Cardell-Fernandez et al. 2002):

- attack by air pollutants
- dissolution in clean rain (karst effect)
- dissolution caused by neutralization of rain acidity

The role of water in contact with carbonate stone is to provide a medium into which the calcium carbonate can get dissolved. During this dissolution, the CO_2 from the air also dissolves in the water establishing the equilibrium of the dissolution reaction as follows:

$$CaCO_3(s) + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

In the absence of other dissolved species, the equilibrium strongly tends to the left.

In tropical climate, water availability is guaranteed by high levels of relative humidity and long rain periods along the year. The presence of high levels of SO_2 in the air promotes the formation of calcium sulfate as reported by Gobbi et al. (1998). Dry deposition of air pollutants (especially SO_2) is the principal process involved in the formation of $CaSO_4$ along with acid rain, which is also an important factor.

1.1 Influence of Pollutants Deposition

In outdoor environments, the major pollutants are acidic particulates and marine aerosols (Cole et al. 2007), which may lead to damage from mineral crystallization and water condensation which provides a culture medium for biodegradation. Within buildings (museums or historic structures), there may be a wide range of particulates and pollutants. Salt weathering is one of the principal causes of deterioration of stonework and masonry used in architectural heritage all over the world. Salt-induced deterioration of architectural heritage is considered to be accelerated drastically in coastal and marine environments (Cardell et al. 2003).

In 1990s, an increase in stone weight loss was reported under the influence of SO_2 for different sites of the UK (Webb et al. 1992; Butlin et al. 1992). Even though in Europe and in the USA the concentration of SO_2 in the atmosphere has sensibly diminished in the last decade, atmospheric material degradation continues, that is why a new multipollutant effect on materials is proposed. A dose–response function from the 8-year ICP materials exposure program has been reported (Kucera et al. 2007). Besides the presence of SO_2 and acid rain, the effects of HNO_3 and particulate material have been included in dose–response functions for metallic materials. NO_2 is not included in any of the functions directly, but is closely related to HNO_3, which is included for limestone. The effect of particulate matter is included for carbon steel, bronze, and limestone.

Preliminary results from an exposure program devoted to determine atmospheric corrosion effects of acidifying pollutants in tropical and subtropical climates of Asia and Africa have been recently published (Tidblad et al. 2007). Limestone degradation after 1 year of exposure is presented together with environmental data (SO_2, NO_2, HNO_3, O_3, particles, amount and pH of precipitation, temperature, and relative humidity) for all the test sites. It is important to note that the highest chloride deposition rate reported is 1.93 mg/m^2 day, indicating that the influence of this deposition could not have significant effects. The degradation observed in the experiments was substantially higher than expected for limestone. The experiment involved 12 test sites in Asia (India, Vietnam, Thailand, Malaysia, and China including Hong Kong) and four test sites in Africa (South Africa, Zambia, and Zimbabwe). It was found that

SO_2 pollution is the most critical factor on limestone degradation together with the correlated effect of pH and HNO_3. Regarding tropical climate, investigations for coastal places are very scarce.

Reaction of stone with gaseous compounds occurs during the absorption process into the porous surface. The oxidation is accelerated at the gas/water interface by the presence of NO_2, but it is clear that NO_2 is only one of the many possible oxidants in urban and rural environments (Massey 1999). In conclusion, there is sufficient evidence that NO_2 could have a role in the oxidation of sulfite.

Anthropogenic particles and natural dust tend to be similarly affected by deposition/soiling and rain washing, which act dynamically as competitive processes (Monna et al. 2008). Examination of archival photographs suggests that soiling predominated in the past, when the air was rich in black dust, whereas equilibrium or even weathering may occur nowadays due to recent improvements or at least changes in air quality, that is, a new multipollutant situation.

1.2 Biodegradation

Rough surfaces and pores provide convenient homes for a variety of organisms, bacteria, algae, fungi, and lichen that colonize stone surfaces forming patinas. Experimental results point to the ability of fungi to proliferate on lithic substrata in the presence of aerosol particulate as nutrient (Moroni and Pitzurra 2008). Recent investigations have found that during the degradation of stones, especially regarding the surface-covering biofilms formed by microorganisms to protect themselves against harmful environmental factors, biodeteriorating effects can be clearly detected in the early stages of stone exposure (Moroni et al. 2004). The combined effect of microbial colonization by fungal growth and atmospheric pollutants in the sulfation of carbonate rocks was investigated. Results indicated a combined action of particulate matter deposition and sulfation in the formation of gypsum on samples exposed outdoor, and to a significant influence of fungal growth in the conversion of metal sulfide particulate matter to sulfate, thus promoting subsequent formation of gypsum also in the absence of pollution.

A report about limestone degradation in archeological sites and historical monuments at the Yucatan Peninsula in Yucatan, Mexico, shows the presence of heterotrophic aerobic and anaerobic bacteria and cyanobacteria in the fortress of Tulum which is located facing the Caribbean Sea and exposed to marine spray and sand erosion (Videla et al. 2000). The weathering of the ruins of Tulum was basically in two types of rocks: red and white limestone, both consisting of calcium carbonate according to X-ray diffraction (XRD) analyses. A major difference is their porosity: white rocks are around 2.5 times more porous than red rocks (Maldonado et al. 1998).

1.3 Influence of Water on Stone Degradation

Water circulation in stones and water flow between stones and atmosphere or ground are one of the main driving factors in the complex degradation processes of historical monuments. It is well known that porous building materials absorb and desorb water as a function of the weather conditions (temperature, relative humidity, and rainwater), that is why water plays a fundamental role in the phenomena of stone deterioration (Becka et al. 2003). Furthermore, the fluxes of water within the stone affect the mechanical behavior of the material and can be responsible for its deterioration.

The weak action of condensed water on the stone surface, particularly if compared with that of rain, is reported by Zendri et al. (2001); however, condensed water facilitates dissolution of pollutants and their chemical action on the stone.

A very important aspect of biological degradation is that this type of damage does not only change the aesthetic aspect of the surface but also, in the case of superior plants, their roots penetrate into the stones and eventually break them, which in case of mechanical elimination of the plants, part of the surface could be destroyed.

1.4 Crusts Formed on Limestone and Mortars Surface

Degradation of calcareous stones frequently occurs in the presence of dust deposited on the rough stone surfaces. The deposits not only change the visual appearance of the stone structure but also enhance the retention of water enhancing degradation processes. In a polluted environment, deposits including dust, biomass, and carbon particles are incorporated into a neo-mineral matrix formed as a consequence of stone interaction with environmental agents forming black crusts. Graedel et al. (2000) reported the presence of bassanite ($CaSO4{\cdot}1/2H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), nitrocalcite ($Ca(NO_3)_2{\cdot}4H_2O$), whewellite ($Ca(C_2O_4){\cdot}H_2O$), and weddellite ($Ca(C_2O_4){\cdot}2H_2O$) in limestone crust composition. Oxalates are the only organic degradation product consistently identified on carbonate stone. They seem to predominate in regions where air pollution is low and biodegradation is generalized. There are at least three sources that can supply oxalate ions to the stone surface: secretions from algae and lichens, degradation of surface pigments or protective compounds and atmospheric particles, and wet deposition. Algae, lichen, and microorganism secretions are very likely the dominant source.

An interesting aspect of carbonate stone degradation is that oxalates and sulfates tend not to be present together; at any rate, their concentrations are not proportional to each other. The explanation is that algae and lichens, apparently the primary source of the oxalate ions, are highly sensitive to sulfur compounds (Graedel 2000).

Black crusts are rarely continuous and impermeable and do not constitute a protective layer for the limestone surface. In fact, the greater solubility and higher porosity of calcium sulfate with respect to calcium carbonate are responsible for water infiltration and recrystallization phenomena; sulfation and degradation processes can continue due to the presence of micro-cracks on the crust surface.

It is reported that under the present climatic conditions in the Mediterranean basin (Garcia-Vallès et al. 1998), erosion is a more active process than deposition, and the crusts and patinas show a tendency to disappear from the surface of the monuments. Analysis of original composition and degradation products of the limestone and the sandstones from the facades of one historical building of Spain showed the presence of carbon particles, gypsum ($CaSO_4{\cdot}2H_2O$), and some nitrate compounds (Martınez-Arkarazo et al. 2007). Chloride and sulfates are not significant soluble salts in the facades of the building, but the amount of nitrate is high in some of the most deteriorated samples and even higher in black crusts.

A black crust sample from the stony central portal of the abbey of St. Denis, France was analyzed to determine whether it was due to atmospheric pollution or to the degradation of a past restoration treatment (Galletti et al. 1997). Stratigraphic surveys by optical microscopy, FTIR, SEM/EDX, and PY/GC/MS were consistent in ascribing the bulk of the crust to gypsum ($CaSO_4{\cdot}2H_2O$) with inclusion of carbon particulate (Gaviño et al. 2004).

1.5 San Francisco de Campeche and Havana Limestone Buildings in Coastal Tropical Climate

The humid tropical climate of Cuba and the Yucatan Peninsula (Mexico) is characterized by an average air temperature always higher than 15°C, frequently high relative humidity, a summer or wet season (May–October) with frequent and heavy precipitations and a winter or dry season (November–April) with lower precipitations, but with increasing atmospheric chloride deposition levels as a consequence of cold fronts coming from the north during the winter. A general map showing the position of the cities of Havana (Cuba) and Campeche (Mexico) is presented in Fig. 1.

The absolute maximum temperature in Cuba is 38.6°C, while a temperature over 40°C is frequently reported in Campeche. Average relative humidity in the west side of Cuba (site where Havana is located) is frequently higher than in San Francisco de Campeche (Havana 80%, Campeche 76%). In spite of this, the classification of time of wetness according to ISO-9223 is the same for the two places: $\tau 4$, corresponding to "Outdoor atmospheres at all climates, excepting dry and cold climates" (ISO 9223:1992).

In the case of Havana and San Francisco de Campeche cities, there is a natural source of airborne salinity for each one: the waters of the Atlantic Ocean and the Gulf of Mexico. Airborne salinity plays an important role in determining corrosivity of the atmosphere (Corvo et al. 2008). It has been determined that in case of metals, corrosivity is higher in Havana with respect to San Francisco de Campeche, due to a higher salinity in Havana.

The old part of Havana is located beside the Havana Bay and near Havana Sea Boulevard, very near the bay seashore. The San Francisco de Campeche historical center is also located in front of the seashore. Hundreds of buildings built with limestone, in most of the cases covered with limestone mortars (made with sand, lime, and calcareous binder), composed the old part of both cities.

In this paper, we will refer particularly to the San Francisco de Asís Minor Basilica and the convent in the old Havana (Fig. 2) and Forts San Pedro and San Carlos in San Francisco de Campeche City (Figs. 3 and 4).

The San Francisco de Asís Minor Basilica and the convent were built at the end of the sixteenth century and rebuild in baroque style in the middle of the eighteenth century. In the present time, the building

Fig. 1 General map showing the position of the cities of Havana (Cuba) and San Francisco de Campeche (Mexico)

houses a museum of religious art, concert, and art expositions hall. The spacious building itself is a wonderful example of eighteenth century architecture and is located approximately 200 m away from the coastline (Fig. 5). The wall of this building bordering Oficios Street is placed in a site where direct influence of sun radiation in the lower part of the building is limited by other buildings located in front of it. The marine breeze coming predominantly from the inner side of the bay, which is probably the most contaminated, goes through the narrow corridor formed by the buildings. Other walls near San Francisco Square are placed in an open ample space, where they receive the influence of marine breeze from the outer side of Havana Bay and direct sun radiation.

On the other hand, Forts San Pedro and San Carlos crowned the northwest and southeast corners of the irregular hexagonally shaped bastion and rampart fortified system surrounded San Francisco de Campeche urban core. Continuous vehicle traffic flows through a street next to the San Carlos building which is located about 100 m away from the shoreline. San Pedro Fort

Fig. 2 Basilica Minor and Convent San Francisco de Asis, old Havana City

Fig. 3 San Pedro Bastion at Campeche

does not receive direct marine aerosol as is the case of San Carlos Fort (see Fig. 6) because it is relatively far from the shoreline (about 1 km). Nowadays, these colonial constructions are surrounded by traffic jammed streets in which intense commercial, cultural, and tourism activities are carried out.

Local calcareous materials including quarried limestone blocks, sand, slake lime, and carbonate clay marls (known as sahacab in Yucatán Mayan language) were combined to erect both forts. Periodic restoration projects carried out in the recent past introduced white and gray cement mortars mixed with pulverized stone as temper. This procedure could cause problem due to inhomogeneous permeability of the building walls.

1.6 Limestone Degradation

Different types of limestone degradation are observed at San Francisco de Asís Minor Basilica and the convent:

- Presence of white spots in chairs and floors of the Basilica as a result of degradation of indoor walls.

Fig. 4 San Carlos Bastion at Campeche

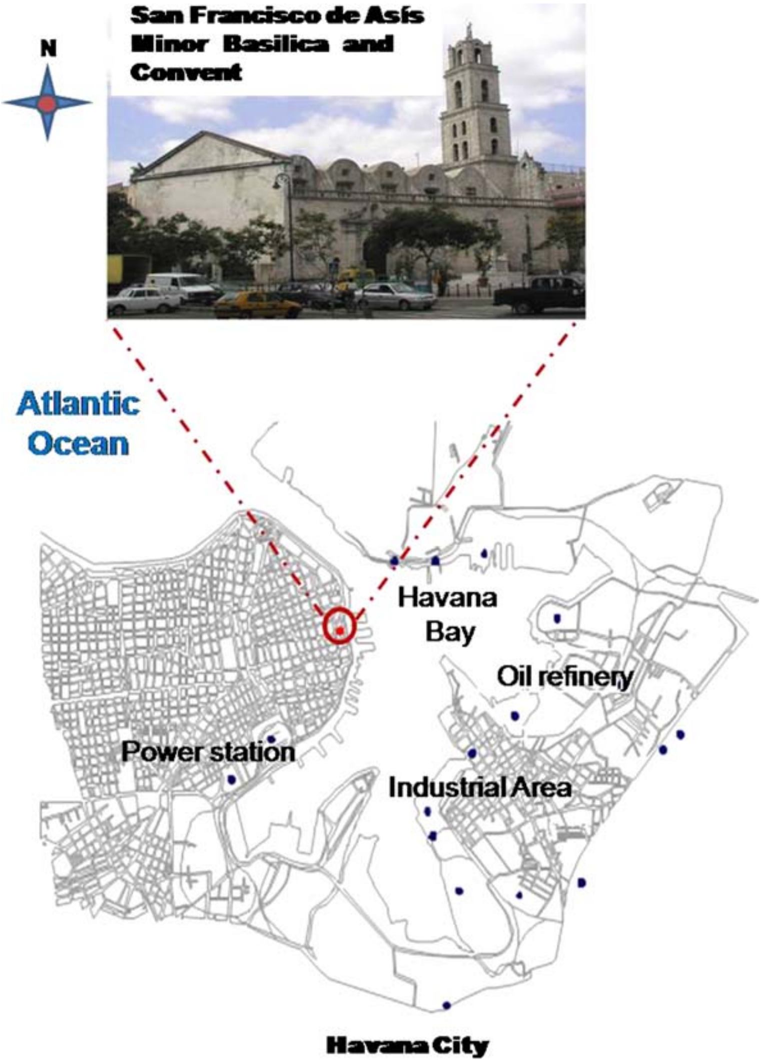

Fig. 5 Map showing the position of the Basilica Minor and Convent San Francisco de Asis in the old Havana City

- Appreciable deterioration of paint coating because of extremely high humidity in the indoor wall corresponding to Oficios Street.
- Black crust in the outdoor facade of the Basilica at Oficios Street. Only in the lower part, where sun radiation does not impact directly and the presence of biological organisms is not observed as shown in Fig. 7. In the last restoration procedure (1999–2000), this black crust was not cleaned. The upper surface of the tower does not present black crusts.
- Growing of plants and other organisms in the wall of the convent corresponding to Oficios Street (Fig. 8). In the last restoration procedure of the building, this wall was cleaned.
- Black crusts and patinas formed on the wall in front of San Francisco Square are probably a mixture of biological and inorganic products (Fig. 9). Patinas are observed as a consequence of water drainage.
- Growing of plants in a column of the inner yard of San Francisco de Asís Convent. This plant destroys the site where it has grown. Similar situations have been observed in windows.

Limestone and mortars degradation at Forts San Pedro and San Carlos:

- Deposits of white, brown, gray, and black crusts can be observed in areas where mortar has lost continuity as a consequence of inhomogeneous permeabil-

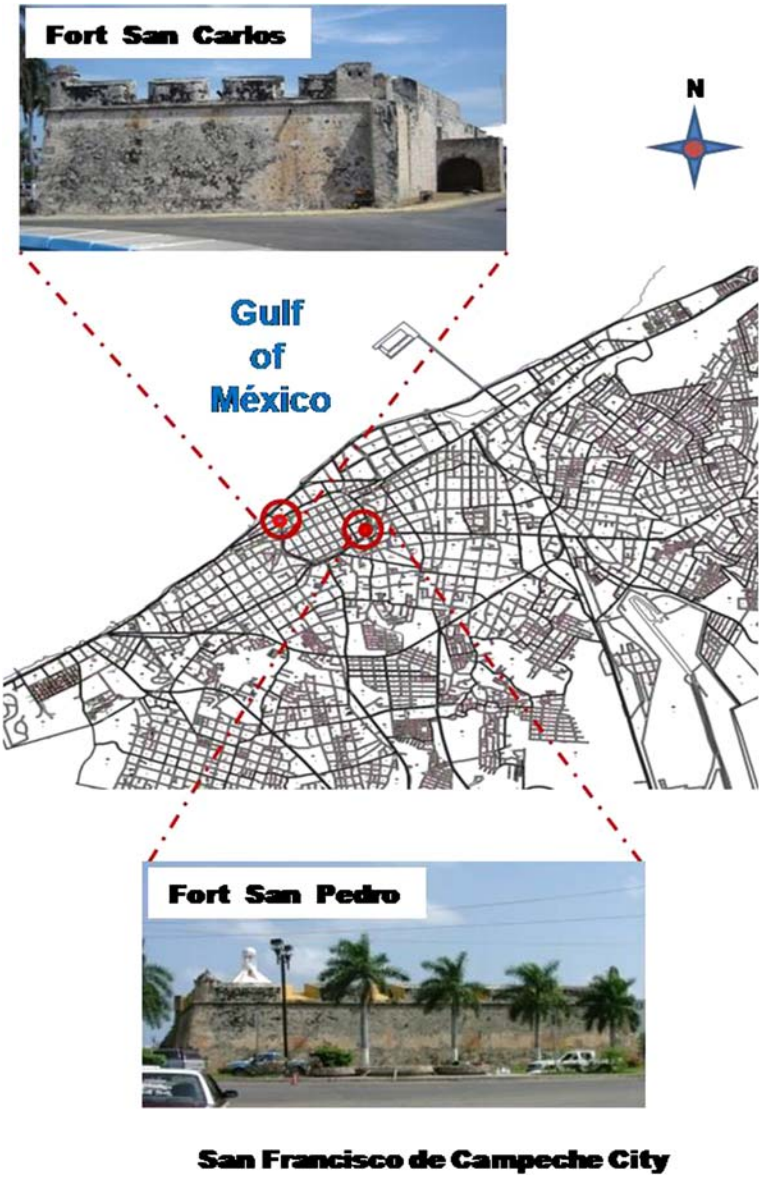

Fig. 6 Map showing the positions of San Carlos and San Pedro fortress in the City of Campeche

ity, mechanical effects caused by human activity, erosion by natural agents, or in zones where there are residual pigments, acting like nucleation center for the growth of crusts (Fig. 10).

- Formation of caverns and cracks because of karst effects and erosion in walls W, S, and E of Fort San Carlos and SE in For San Pedro (Fig. 11).
- The use of Portland cement mortars in recent restoration works induces changes in permeability properties of rocks and mechanical stresses. It is not compatible with rock and traditional mortars. It can induce cracks formation and losses of components (Fig. 12a–d).
- Traditional mortars without enough consolidating properties fall down (Fig. 13).
- General microbial colonization inducing the formation of patinas in walls and stone blocks of vortices, doors, watchtower, and access ramps in both buildings.
- Presence of plants is observed in some places of these two fortresses, where mortars have fallen off.

Fig. 7 Facade of Basilica Minor at Oficios Street. Black crust in the *lower part*. No crust observed in the tower

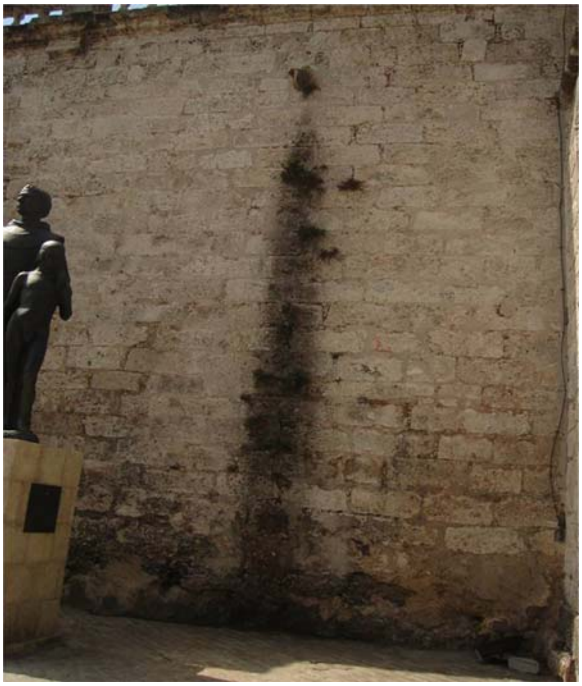

Fig. 9 Basilica Minor San Francisco de Asis, San Francisco Square wall. Patina formed due to water drainage

2 Experimental Part

2.1 Test Sites

Test sites selected for atmospheric contamination evaluation in Campeche State, Mexico were the following:

- National Institute of Anthropology and History Center (INAH), located at the center of the historical city of San Francisco de Campeche. The test site was placed in the roof of this building. The evaluations carried out began on February 2007 and finished on January 2008 for air pollutants and from February 2006 to December 2007 for rain.
- Dzibilnocac Mayan ruins, located at about 180 km to the east of San Francisco de Campeche City. Evaluation was carried out beginning February

Fig. 8 Oficios Street wall, Convent San Francisco de Asis. Presence of plant and development of biological patina

Fig. 10 Presence of crusts having different colors at San Carlos Bastion

2007 up to January 2008. Rain pH was not determined.

- Calakmul Ecological Reserve, far from any human industrial or urban development, located close to the borderline with Guatemala, about 350 km southeast to San Francisco de Campeche City. Evaluation was carried out beginning February 2007 up to January 2008. Rain pH was determined beginning August 2006 up to July 2007.

Fig. 11 Example of Carsick structures provoked by water infiltration observed at San Pedro and San Carlos fortress

In the city of Havana, atmospheric contamination was determined in four test sites:

- San Francisco de Asís Minor Basilica and Convent (indoor conditions), less than 200 m from Havana Bay shoreline. Under indoor conditions, the deposition rate is usually considerably lower than outdoors. Two measurement points were placed indoor, inside the Basilica, in the concert hall at about 3 m from the floor, and in the Chorus, in the same Basilica building, at about 10 m from the floor. Evaluation was carried out beginning September 2006 up to March 2007. No rain was determined because the sites were placed indoor.
- Casa Blanca, located in the other side of Havana Bay, more than 2 km from the open shoreline and about 200 m from the bay shoreline, less than 3 km from the Basilica. At this site, atmospheric pollutants were determined in the period August 1998–March 1999. Very probably, the present contamination level should have differences as a function of the measuring period; however, during that time, Basilica Minor and the convent received the contamination and crusts formed, particularly at the Oficios Street Basilica wall. Black crust was not eliminated during the last conservation procedure,

Fig. 12 a–d Use of Portland cement mortar at San Carlos fortress

Fig. 13 No consolidation between stone substrate and mortar at San Carlos fortress

so crust should be formed on those conditions. Rain pH was determined for a 10-year period (1995–2004).

- Via Blanca corrosion station, located less than 200 m from the bay shoreline, more inside into the bay, at about 2 km from the Basilica Minor and Convent San Francisco de Asis. At this site, pollution data were obtained during the January 1989–January 1999 period. Very probably, the present contamination level should have differences with respect to the measuring period; however, during this time, San Francisco de Asís Basilica Minor and the convent were under the influence of atmospheric pollution and crusts were formed. Particularly, at the Oficios Street Basilica wall, black crust was not eliminated during the last conservation procedure and should be formed on those conditions. Rain pH was not determined.

2.2 Evaluation of Atmospheric Contamination

Atmospheric pollutants determined were the following:

- Deposition rate of sulfur compounds by sulfate passive samplers was according to ISO 9225 (1992). Determination of sulfur compounds in Campeche was carried out by the sulfation plate method.
- Determination of sulfur compounds in Cuba was carried out by alkaline plates (included also in ISO 9225 standard).
- It is important to note that these two methods for the determination of the deposition rate of sulfur compounds are sensible to all types of sulfur compounds, that is, SO_2, SO_3, SH_2, sulfates, and others.
- Chloride deposition rate was determined by using passive methods according to ISO 9225, the wet candle method in Campeche sites, and the dry plate in Cuban sites (Corvo et al. 1995).
- Nitrogen oxides using diffusive samplers (UNE EN 13528). Diffusion tubes consisted of acrylic tubes containing two stainless steel meshes impregnated with triethanolamine solution (35%) as collecting media. The tubes are exposed for 30 days (±5) to the environment. Afterwards, meshes are taken and nitrogen oxides extracted by complex formation with sulfanilamide and naftilendiamide solution. Quantitative analysis is carried out using UV/Visible spectrophotometer at 540 nm.
- At Campeche, rain samples were collected by using an automatic wet/dry sampler equipment according to recommendations of the National Acidic Deposition Program of the United States of America (NADP 2000). In Havana, manual collection of samples was carried out. pH was determined in the two countries. The rain pH was calculated considering the average month pH/total amount of rain during the period.

2.3 X-ray Diffraction Analysis

Limestone and mortar crust representative samples were taken from the walls of the three selected buildings, kept in a plastic bag, and stored until the analysis was carried out. The samples were ground, introduced in a Bragg–Brentano geometry X-ray diffractometer (Siemens D5000), and analyzed under the following conditions: Cu Kα radiation (λ= 1.5416 Å) and operational conditions of 25 mA and 35 kV at a step size of 2°/2θ/min in the 2–60° range 2θ.

2.4 Temperature and Humidity Determinations

Temperature and humidity were determined using data loggers from selected walls of San Francisco de Asís Minor Basilica and Convent. Air temperature and relative humidity were measured every 30 min and processed to obtain average, maximum, and minimum monthly data.

3 Results and Discussion

Table 1 shows the results of atmospheric contamination measured in Campeche and Havana cities. It can be noted that there is an evident difference in the deposition level of sulfur compounds between Havana and Campeche sites. Havana sites show a significant higher deposition of sulfur compounds compared to Campeche. All Havana sites are classified as P_1 (urban atmosphere) according to ISO 9223 Standard. Regarding Campeche sites (including Calakmul), they are classified as Po (rural atmosphere-SO_2 deposition rate least than 10 mg m^{-2} day^{-1}). Classification of Campeche City corresponded to a rural place, a small city with 0.28 million inhabitants.

About chloride deposition, there is a different situation. Indoor sites presented, as expected, negligible presence of chlorides. It is in agreement with the

Table 1 Atmospheric contaminants (sulfur compound deposition, chloride deposition, and NO_2 concentration) determined at different sites of Campeche and Havana

Country and State or City	Site	Exposure conditions	Sulfur compound DR (mg/m^2 day)			Class ISO 9223	Chloride DR (mg/m^2 day)			Class ISO 9223	NO_2 concentration (μg/m^3)		
			Average	Max	Min		Average	Max	Min		Average	Max	Min
Mexico, Campeche	INAH	Outdoor	1.53	3.52	0.87	Po	23.43	32.07	13.20	S1	9.70	15.79	4.7
	Dzibilnocac	Outdoor	1.59	3.61	0.12	Po	11.99	23.08	5.95	S1	2.12	4.62	1.0
	Calakmul	Outdoor	0.54	1.03	0.03	Po	5.15	8.76	1.95	S1	0.47	0.88	0.23
Cuba, Havana	Basilica	Indoor	10.50	12.50	6.51	P1	Negligible	–	–	So	16.35	26.08	6.23
	Chorus	Indoor	11.60	14.65	7.6	P1	Negligible	–	–	So	16.29	24.49	11.5
	Via Blanca	Outdoor	30.34	65.40	9.60	P1	17.85	198.20	1.10	S1	–	–	–
	Casa Blanca	Outdoor	24.57	41.60	8.20	P1	10.23	17.40	3.30	S1	–	–	–

data previously reported (Corvo et al. 2007). The levels of chloride deposition for outdoor sites are the same for Havana and San Francisco de Campeche cities (S1). It should be taken into account that both cities are located close to the seashore. Although Havana presents a significantly higher chloride deposition rate compared to San Francisco de Campeche (Corvo et al. 2008), in the site corresponding to San Francisco de Asís Minor Basilica and Convent, due to the influence of the surrounding buildings and the location close to the bay and not to the open sea, chloride deposition is lower than in other places and similar to the one found in Campeche. Under these conditions, the influence of airborne salinity in degradation phenomena of historic building in both cities should be very similar.

A different situation is observed in the case of NO_2: indoor Havana sites show a higher concentration than outdoor Campeche sites. It means that outdoor concentration in Havana should be significantly higher than in San Francisco de Campeche. It is confirmed with the data reported for a site placed in the historical center of the old Havana at a distance of about 1 km from the San Francisco de Asís Minor Basilica and Convent. Monthly NO_2 concentration determined was between 30.83 and 39.05 μg/m^3 during 2007 (Valdés et al. 2008).

Atmospheric pollution in San Francisco de Campeche City is significantly lower than in Havana City. As the two cities are placed beside the sea, both have the influence of chloride deposition. NO_2 concentration at INAH station is higher than SO_2 deposition, which means that a multipollutant effect with the additional inclusion of a natural contaminant, chloride, is taking place on stone degradation, as proposed by Kucera et al. (2007). Under these conditions, SO_2 levels are low and the influence of NO_2 could increase. Dzibilnocac has a clean atmosphere, only with a small contamination and the presence of low levels of chlorides. Calakmul has a very clean atmosphere, although chloride ions are present in a small deposition rate.

Regarding Havana, the influence of SO_2 is significant; however, NO_2 concentration is also relatively high. At this site, the influence of SO_2 could make possible the formation of calcium sulfite in reaction with limestone and a subsequent oxidation to gypsum under the influence of NO_2 and perhaps other oxidants. These conditions represent also a tendency toward a multipollutant effect on stone degradation, always under the presence of airborne salinity. At indoor conditions, a significant degradation of stone could occur because significant sulfur compounds deposition and high NO_2 concentration are reported for Basilica and Chorus (in addition to a high humidity). The presence of white stains is observed probably corresponding to stone powder on the chairs placed on the Basilica.

It is reported that acid rain plays an important role on limestone degradation. A comparison of rain pH between INAH sampling sites at San Francisco de Campeche City and Calakmul (Campeche), and Casa Blanca site (Havana), is presented in Table 2. It is important to note that rain pH is higher for Campeche sites compared to Havana sites, in agreement with the presence of higher atmospheric pollutant levels in Havana sites. It means that in Havana City, higher

Table 2 Evaluation of rain pH determined at Campeche and Havana sites

Country and state or city	Site	Period of evaluation	Rain pH		
			Average	Maximum	Minimum
Campeche, Mexico	INAH	Feb/06–Jan/07	6.0	6.66	5.28
	INAH	Feb/07–Dec/07	6.53	7.80	5.12
	Calakmul	Aug/06–July/07	5.76	6.75	5.15
Havana City, Cuba	Casa Blanca	1995–2004	5.42	5.8	5.1

stone degradation rate should be expected. In addition, the average rain pH at Campeche shows values higher than normal rain, and it could be probably due to the presence of calcium carbonate particles in the air. Predominant winds at Campeche City come from the land to the sea, where wind can bring carbonates and other basic particles from the soil which tends to neutralize the rain acidity. In another way, it seems that in tropical latitudes, abundant rain precipitation induces dissolution of limestone and mortar components by karst effect, increasing deterioration.

3.1 Crust Phase Identification

In San Francisco de Asís Basilica Minor and Convent, calcite is the main phase contained in limestone. Small quantities of quartz, gypsum, and magnesium silicate were also determined (see Table 3).

Black crusts formed at the Basilica facade in Obispo Street show gypsum as a predominant phase with small amounts of calcite and quartz. It means that black crust composition is almost completely gypsum due to contamination by atmospheric SO_2. Basilica surface was not cleaned in the last restoration procedure (1999–2000), so this crust was formed several years ago. No black crust is formed in the same street at the wall of the convent (this surface was cleaned in the last restoration procedure). It is important to note that black crust is formed only in the lower part of the Basilica surface. No black crust is observed in the upper side where sun and wind reach directly the surface. This situation suggests that perhaps black crust has been formed due to the presence of almost permanent high humidity in the lower surface of the Basilica. This humidity has allowed the occurrence of sulfur compound reactions. Deposition of higher sulfur compounds should occur during the day, when the upper surface of the Basilica is dry, so the formation of the black crust is more difficult.

Crust formed at Fort San Carlos is mainly formed by calcite, the original main content of the stone. Different minor phases are: aragonite, dolomite, and quartz (Table 4). The presence of whewellite and weddelite in the samples is an index of the influence of biological activity in stone deterioration, although the presence of bassanite shows the influence of environmental SO_2.

Crust obtained from Fort San Pedro (Table 4) shows the presence of calcite as a principal constituent together with other components—whewellite and weddelite; gypsum, a primary product of the influence of environmental SO_2; sodium feldspar; portlandite; goethite; and hydroxyapatite—probably components added as part of mortar composition.

XRD analysis of crust composition shows significant differences between San Francisco de Asís Basilica Minor and Convent and San Francisco de

Table 3 Results of XRD phase analysis of limestone and black crust formed on the surface of the facade of Basilica Minor San Francisco de Asis at Oficios Street

Material	Main phase	Minor phases
Limestone obtained from Basilica Minor San Francisco de Asis	Calcite $CaCO_3$	Gypsum $CaSO_4{\cdot}2H_2O$ Quarz SiO_2 Proto-enstatite (magnesium silicate) $MgSiO_3$
Crust obtained from the facade of Basilica Minor San Francisco de Asis, Oficios Street	Gypsum $CaSO_4{\cdot}2H_2O$	Calcite $CaCO_3$ Quarz SiO_2

Table 4 Results of XRD phase analysis of crusts obtained from the surface of San Carlos and San Pedro Forts at the old city of Campeche

Material	Main phase	Minor phases
Crust obtained from San Carlos Fort	Calcite ($CaCO_3$)	Aragonite ($CaCO_3$), sodium feldspar ($Na_2Si_4O_9$), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), whewellite ($Ca(C_2O_4)\cdot H_2O$), bassanite ($CaSO_4\cdot 1/2H_2O$), weddellite ($Ca(C_2O_4)\cdot 2H_2O$), portlandite($Ca(OH)_2$)
Crust obtained from San Pedro Fort	Calcite ($CaCO_3$)	Aragonite ($CaCO_3$), sodium feldspar (($Na_2Si_4O_9$), quartz (SiO_2), dolomite ($CaMg(CO_3)_2$), goethite (FeOOH), whewellite($Ca(C_2O_4)\cdot H_2O$), weddellite($Ca(C_2O_4)\cdot 2H_2O$), portlandite ($Ca(OH)_2$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), gypsum ($CaSO_4\cdot 2H_2O$)

Campeche's fortress crusts. In the Cuban building, the main mineral phase is gypsum, showing the importance of atmospheric sulfur compounds in crust formation mechanisms and limestone degradation at Havana City. The influence of microorganisms in crust formation seems to be not important in this wall. The forts of San Carlos and San Pedro show some signals of the influence of atmospheric sulfur compounds and biological activity, but the main mechanisms of crust formation are controlled by water dissolution and recrystallization of calcium carbonate. The results are in agreement with the levels of air pollution: The presence and influence of air pollution on limestone degradation is higher in Havana than at Campeche.

3.2 Influence of Humidity on Stone Degradation

Limestone degradation is accelerated under high humidity conditions. As a first effect, the development of biological organism is enhanced, depending on the characteristics of the substrate. Second, atmospheric pollutants can be dissolved easier in the humidity existing in the porous material, and lastly, if the water flow inside the stone is not homogeneous, cracks could appear due to differences in permeability.

The influence of human behavior is important in this situation because if attention is not given to the defects in the building, an increase of inhomogeneities in water content in the stone could accelerate stone degradation. That is the case for the convent wall at Oficios Street. The roof of the convent building adjacent to Oficios Street is in bad condition and does not protect against rain. When it is raining, water runs inside and through the indoor wall, which is the reason why paint coatings in indoor rooms are deteriorated. Another example is a bathroom in the fourth floor that presents plumbing problems and almost continuously has a water flow discharging on Oficios wall. Under these conditions, humidity of the wall is very high. It favors the growth of biological organisms, including plants. A comparison of temperature and humidity data for Oficios, San Francisco Square, and Avenida del Puerto Street (this last wall does not show appreciable deterioration problems) shows significant differences (see Table 5). Oficios Street shows higher humidity during wet and dry climatic seasons, followed by San Francisco Street. In the last one, the presence of biological organisms is lower, but relative humidity is still high, probably due to bad conditions of the roof, but not so appreciable as

Table 5 Temperature and relative humidity for the convent wall at Oficios Street, Basilica wall at San Francisco Street, and convent wall at Avenida del Puerto Street

Wall	Temperature (°C)			Relative humidity (%)			Measuring period
	Average	Max	Min	Average	Max	Min	
Convent wall (Oficios Street)	29.4	30.9	29.2	81	88	84	Wet season (May to October)
	23.6	25.3	22.2	93	98	90	Dry season (January to April)
Basilica wall (San Francisco Street)	27.1	31	28.7	60	79	69	Wet season (May to October)
	24.1	26.5	22.5	72	84	64	Dry season (January to April)
Convent wall (Avenida del Puerto street)	28.5	31.1	28.9	63	74	67	Wet season (May to October)
	24.8	27.6	22.9	65	73	59	Dry season (January to April)

in Oficios; however, relative humidity at Avenida del Puerto Street does not show high values, with no significant deterioration problems.

As can be observed, biodegradation is the main factor affecting the convent wall at Oficios Street. Taking into consideration that the influence of sun radiation at this narrow street is lower, these two conditions—increase of humidity due to defects not yet repaired and decrease in the influence of direct sun radiation—provoke conditions that enhance biodegradation. No inorganic crusts are observed. In other walls of the convent or Basilica, a lower biodegradation is observed because they are submitted more directly to the influence of sun radiation and present a lower humidity.

With regard to the San Carlos fortress, the use of cement mortars could have caused differences in water permeability across the wall. This situation could cause cracks and falling of mortar parts in the wall. Growing of plants is observed at San Carlos and San Pedro walls. Other important phenomena observed in the walls of both buildings are karst structures provoked by water infiltration across masonry during rainy season. The massive structure in both buildings is an artificial rocky outcrop, across which rain water fluid causing dissolution and erosion of stone and mortar components takes place. During this process, cracks and small cavities are formed inside the masonry. Water fluids forming drainage structure can be observed in walls of the buildings (Fig. 11). White to dark brown deposits are formed over mortar and stone in the near of water drainage discharge. According to XRD analysis, these deposits are rich in calcium carbonate, as a probable consequence of calcium carbonate recrystallization.

4 Conclusions

1. Air contamination levels in Havana sites are higher than in San Francisco de Campeche. The influence of airborne salinity is present in the two cities located in tropical coastal climate.
2. Campeche shows pollution levels according to a multipollutant situation, but always with the additional presence of airborne salinity. Dzibilnocac and Calakmul sites can be considered to have clean atmospheres (always under the influence of low levels of airborne salinity).
3. A higher pollution in Havana is the cause of black crust formation (composed mainly of gypsum) at the facade of San Francisco de Asís Basilica Minor. It is formed in the part of the facade where direct influence of sun radiation is lower, that is, in conditions where wet/dry cycles are near to indoor conditions, but under the influence of outdoor pollutants, humidity, and rain. Under the direct influence of sun radiation and wind (bell tower), no black crust formation was observed.
4. The presence of oxalates at Campeche crusts shows that biodegradation is an important mechanism in these conditions.
5. The higher humidity of the wall of the convent at Oficios Street causes a significant biodegradation. The influence of air pollution is not very significant despite relatively significant pollution levels.
6. Water infiltration causes the formation of caverns and small cracks at San Pedro and San Carlos walls.
7. The influence of water and humidity enhances the development of biodegradation. Reparation and maintenance defects significantly increase the possibilities of degradation.

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