ACID DEPOSITION EFFECTS ON ARCHEOLOGICAL MONUMENTS IN MEXICO

Humberto Bravo A.[a,*], Rogelio Soto A.[a,b], Rodolfo Sosa E.[a], Pablo Sánchez A.[a], Ana Luisa Alarcón J.[a], Jonathan Kahl[c], Jaime Ruíz B.[a]

[a]Environmental Pollution Section, Center for Atmospheric Sciences, National University of Mexico, Circuito Exterior, Ciudad Universitaria, Mexico, D.F., 04510, Mexico

[b]Division of Basic Sciences, Engineering Faculty, National University of Mexico, Circuito Exterior, Ciudad Universitaria, Mexico, D.F., 04510, Mexico

[c]Department of Mathematical Sciences, University of Wisconsin-Milwaukee. P.O. Box 413, Milwaukee, WI 53201

[*]Corresponding author. Tel.: +52-5616-0701; fax: +52-5622-4052
E-mail address: hbravo@servidor.unam.mx (H. Bravo A.).

ABSTRACT

Effects of acid deposition on monuments by natural weathering or by man made pollutants are well known. Recently, interest in materials damage has included the effects of acid precipitation, in addition to the effects of gaseous and particulate air pollution.

Tajin and Maya archeological zones, in Veracruz, Tabasco, Campeche, Quintana Roo and Yucatan, Mexico, has a great cultural and historical value for mankind. However, there is a great concern on the potential effect of acidic deposition on these monuments because their building material is mainly calcium carbonate. It is known, also, these monuments are surrounded by atmospheric pollution sources (power electric plants, refineries, off and on shore oil exploitation, etc.). To know better the effects on the monuments, besides the pollution sources, it is fundamental to investigate the pathways of pollutants air parcels follow after these pollutants are emitted by the sources.

To know the frequency and characteristics of the acid wet deposition on these areas, two monitoring rain collectors were installed and operated during different years (Tulum, Quintana Roo: 1994-1995 and Tajin, Veracruz: 2002-2004). Once the characteristics of the deposition were determined, an experimental accelerated deterioration chamber was used to quantify the potential effects of acidic precipitation on Tulum and Tajin.

Slabs of limestones were exposed to synthetic acid rain, prepared in the laboratory, according to the chemical composition of natural rain from those sites. Climate condition of these sites were set up to match those found in the field. Superficial recession was also determined on both sites.

Keywords: Tajin, Tulum, acid rain, calcium carbonate, chemical dissolution mechanism, experimental rainfall simulator chamber

1. INTRODUCTION

The impact of acid deposition on the weathering of carbonate stone has been recognized for long time (Lipfert, 1989; Webb et al., 1992; Camuffo, 1992; Reddy, 1987). Recently, the role of acid and acidifying air pollutants has become the cause of considerable concern at both national and international level. This concern has centred mainly around the harmful effects associated, among other things, with acid deposition and serious damage to historical monuments.

It is known that three classes of mechanisms are involved in the stone damage by air pollution (Irving, P., 1991):

a) Aqueous dissolution reactions of calcium carbonate. Carbonate stone (limestone and marble) are particularly susceptible to acidic precipitation due to the dissolution of calcium carbonate with hydrogen ions in aqueous solutions. These solutions can be deposited by rain, dew, mist or fog.

b) Gaseous deposition processes. There are some important gaseous pollutants, like sulphur dioxide, that contributes to rain acidity and lead to formation of commonly observed gypsum in surface crusts.

c) Particle deposition on stone surfaces. Some particulate pollutants may catalyze some processes to make them more effective to produce a more accentuated damage on the stone surface.

The first of these factors, has been studied extensively and the carbonate stone recession has been to focused from several viewpoints, such as: weight loss measurements of stone, chemical analysis of run-off solutions, direct measurement of recession using a microerosion meter, etc. Although this is not the only mechanism responsible for deterioration of carbonate stone, its knowledge is crucial to understand how it affects the atmosphere to this material so important in the construction industry.

The occurrence of acid deposition on Mexican Monuments (Tajin and Tulum) has been shown through a research carried out at the Environmental Pollution Section at the Center for Atmospheric Sciences, National University of Mexico (Bravo et al., 1998, 2000 and 2004).

2. DESCRIPTION OF TAJIN ARCHEOLOGICAL ZONE

Tajin archeological zone is located at the Papantla de Olarte municipality , in Veracruz, Mexico. Its geographic coordinates are 20^0 $28^’$ 35” north latitude and 97^0 22’ 39” west longitude. It is situated 100 m above sea level, and its surface is 1056 ha.

Tajin was one of the most important cities that existed in the Mesoamerica gulf zone. Its beginning date back to 1000 B.C., when the zone started to be inhabited by their first settlers, perhaps Olmecas. The first constructions date back to 100 A.D., and from 600-1150 A.D., the city reached its maximum greatness.

Tajin was also the most important ceremonial centre in Mexican Gulf zone, a place, although, it had not military and economic supremacy, it was very important because of its architecture and engineering (Zaleta, 2001).

Fig. 1 shows where the Tajin is located.

Fig. 1. Map showing Tajin location.

3. EXPERIMENTAL

3.1 PHYSICAL TESTS

3.1.1 X-RAY DIFFRACTION

A limestone sample from Tajin was delivered to the Institute of Research of Materials, National University of Mexico, to carry out the x-ray diffraction analysis. Such analysis were performed with a Bruker-axs D8-Advance Powder Diffractometer, Diffplus B_S software and ICDD data base.

Three components were identified with the following percentages (semiquantitative analysis):

- Calcite (81.2%).
- Quartz (17.9%).
- Feldspar (0.9%).

3.1.2 DENSITY, POROSITY AND WATER ABSORPTION

Three limestone slabs were cut from the crude sample brought from the Tajin and all their faces were polished to eliminate the superficial dirt. Density and water absorption of carbonate stones were determined according procedures by NMX (1986). Porosity was determined according ISRM (1979). Table 1 shows the results obtained.

Table 1. Density, porosity and water absorption from three limestone samples from the Tajin.

Sample No.	Surface (cm^2)	Density (g/cm^3)	Porosity (%)	Water absorption (%)
1	21.34	2.39	9.95	1.60
2	20.51	2.36	11.08	1.53
3	20.25	2.37	10.70	1.65
Mean ± *MSD	20.70 ± 0.40	2.37 ± 0.01	10.58 ± 0.41	1.59 ± 0.04

Mean: Arithmetic Mean

*MSD: Mean Standard Deviation

3.2 DEPOSITION SAMPLING STATION

The deposition sampling station is located at the Tajin on a grass covered area, in order to avoid the pollution of the rain samples by dust and airborne particles. Such station complies with the EPA site selection criteria of precipitation sampling sites of a regional station type. The wet/dry collector used is an automatic Aerochem Metrics Collector. Figure 2 shows a picture of the sampling station.

Fig. 2. Deposition sampling station at the Tajin.

3.3 pH VALUES OF RAIN SAMPLES AT THE TAJIN

From august 18, 2002, to april 9, 2003, 40 rain samples were collected at the Tajin. From these samples, 34 were found to have values smaller than 5.6 (rain pH in equilibrium with atmospheric carbon dioxide (Reuss, 1977)). Figure 3 shows the weighed pH values (superior limit of the rectangles), as well as the minimum and maximum pH values found monthly. Also is shown the samples number analyzed for each month. The weighed pH values were determined according the following equation:

$$\text{Weighed pH value} = -\log\left[\frac{\sum\left[H^{+}\right]V_{pp}}{\sum V_{pp}}\right]$$

where $\left[H^{+}\right]$ and V_{pp}, represents the hydrogen ion concentration and the measured precipitation volume, respectively, for each sample.

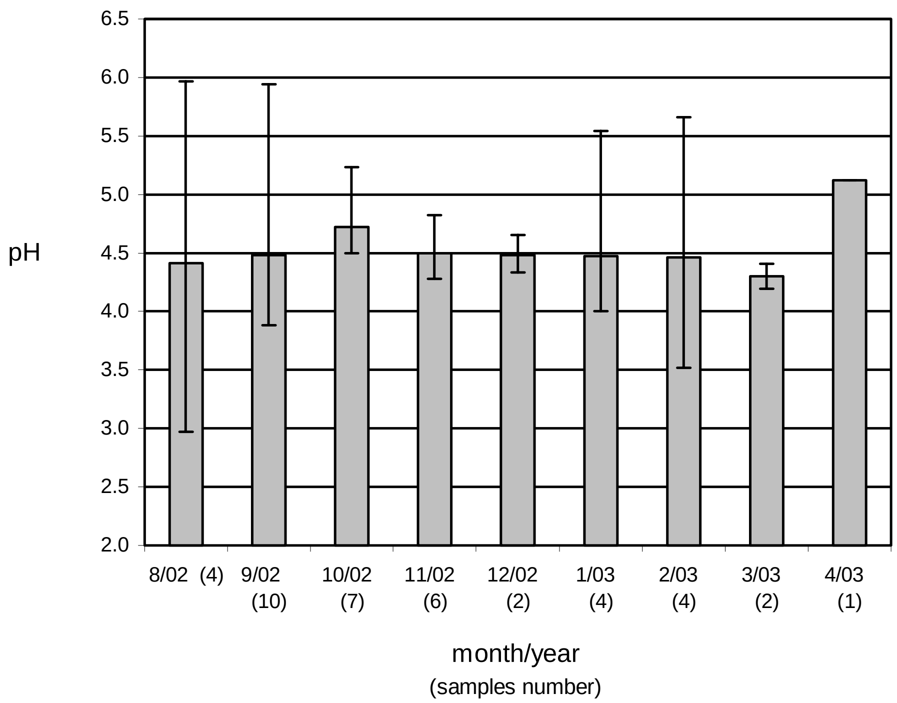

Fig. 3. Minimum, maximum and weighed pH values found in rain samples at the Tajin from august 18, 2002 to april 9, 2003.

3.4 Dissolution of calcium carbonate from limestone by acid rain

In order to know the dissolution mechanism involved when a limestone sample is in contact with acid rain, an experimental rainfall simulator chamber (the description of the chamber and its operation principle are shown elsewhere (Bravo et al., 1998)) was used to simulate the deterioration effect on the material.

Artificial rain solution was prepared in the laboratory with the weighed ionic concentrations similar to those measured at the Tajin area from august 18 to october 11, 2002. Only this period was taken in account to prepare the artificial acid rain solution. Table 2 shows the concentrations of major cations and anions found in such rain samples.

The pH of artificial acid rain was adjusted to 4.4, which represents the lowest weighed value found in the rain samples at the Tajin, during those months.

Ion	Concentration (ppm)
Na^{+}	0.28
K^{+}	0.12
NH_4^{+}	0.30
Mg^{2+}	9.6×10^{-4}
Ca^{2+}	0.24
Cl^{-}	0.49
NO_3^{-}	0.72
SO_4^{2-}	0.66

Table 2. Weighed concentrations (ppm) of major cations and anions in rain samples collected at the Tajin, from august 18 to October 11, 2002.

Inside the chamber were placed three stone samples (each of 20 cm^2 approx.). One year of rainfall was simulated, during 28 h., 750 mL of artificial rain fell down on the limestone samples at a dropping rate of 0.45 mL/min (annual precipitation at Tajin is 1180 mm/year, approx.).

A blank using destilled water as a rain was run simultaneously with the samples.

The following analysis were carried out to the effluent of each sample and the blank: pH, conductivity, cations content (Na^{+}, K^{+}, NH_4^{+}, Mg^{2+} and Ca^{2+}) and anions content (Cl^{-}, NO_3^{-}, SO_4^{2-} and HCO_3^{-}) by HPLC. From these figures, calcium and bicarbonate net concentrations could be determined, during the simulated time study lasted (ten years).

Table 3 shows net accumulative mol number for calcium and bicarbonate ions, for each year, and the corresponding graph is shown in figure 4.

Year	Sample 1	Sample 2	Sample 3
1	0.81	0.87	0.80
1	*2.36*	*1.09*	*2.13*
2	1.45	1.29	1.24
2	*3.77*	*2.10*	*3.10*
3	2.18	2.02	1.80
3	*5.17*	*3.50*	*4.23*
4	2.90	2.66	2.34
4	*6.42*	*4.78*	*5.27*
5	3.53	3.34	2.95
5	*7.66*	*6.01*	*6.32*
6	4.34	4.01	3.54
6	*9.12*	*7.17*	*7.41*
7	5.09	4.76	4.08
7	*10.57*	*8.53*	*8.54*
8	5.81	5.46	4.68
8	*12.01*	*9.71*	*9.76*
9	6.54	6.13	5.42
9	*13.32*	*10.94*	*11.03*
10	7.16	6.73	6.13
10	*14.36*	*11.84*	*12.18*

Table 3. Calcium net accumulative mol number (normal type) and bicarbonate net accumulative mol number (*cursive type*) in the effluent of the experimental rainfall simulator chamber. Study simulated time: ten years.

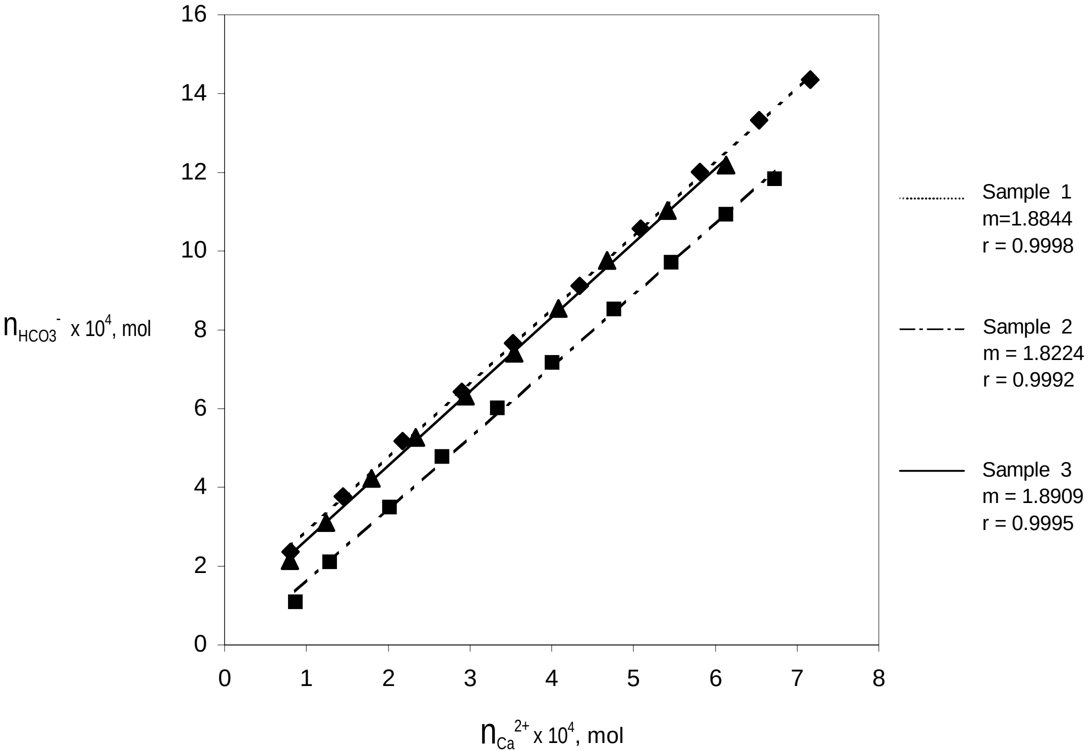

Fig. 4. Relation between the bicarbonate ion net accumulative mol number and calcium ion net accumulative mol number during dissolution of three limestone samples by acid rain.

3.5 CALCIUM CARBONATE CONTENT IN THE LIMESTONE SAMPLE BY REACTION WITH NITRIC ACID

A limestone powder sample was placed in a crucible and dried overnight to 110 ^{0}C. After this, it was placed in a dessicator for 2 h. After the crucible had reach to room temperature, it was weighed until constant weight was attained. From this powder, three samples were weighed, each in a crucible, and they were mixed with high purity diluted nitric acid, until reaction was complete. A nitric acid blank was also run for comparison. The residue was thoroughly washed with deionized water and evaporated for dryness. This operation was made two times more. Finally, the residue was dried in a oven for 2 h., and placed in a dessicator until constant weight was attained.

Table 4 shows the difference in weight after and before of the treatment with nitric acid for each sample and the blank.

Sample No.	Initial weight (mg)	Final weight (mg)	Weight difference (mg)
1	20.3	30.2	9.9
2	20.5	30.6	10.1
3	20.6	30.9	10.3
blank	-	-	constant weight was observed

Table 4. Difference in weight found in three limestone samples by effect of nitric acid.

4 RESULTS

- **4.1 CALCIUM CARBONATE CONTENT IN THE LIMESTONE SAMPLES**
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When the limestone sample was dissolved with nitric acid, the following reaction occurred:

$$CaCO_3 + 2\ HNO_3 \rightarrow CO_2 + Ca(NO_3)_2 + H_2O$$

As the reaction shows, only calcite is dissolved by the acid. It is well known quartz is resistant to acids (Cotton and Wilkinson, 1975; Dana, 1946). If it is considered that limestone sample contains only calcite (c) and quartz (q), the limestone sample initial weight will be:

$$m_i = m_c + m_q$$

By the other hand, after reaction occurred, the weight will be:

$$m_f = m_n + m_q$$

where m_n denotes formed calcium nitrate weight.

According to the stoichiometry reaction and the weights before and after the reaction, the following relations can be written:

Sample 1: $m_c + m_q = 20.3$ mg ; $1.64\ m_c + m_q = 30.2$ mg

Sample 2: $m_c + m_q = 20.5$ mg ; $1.64\ m_c + m_q = 30.6$ mg

Sample 3: $m_c + m_q = 20.6$ mg ; $1.64\ m_c + m_q = 30.9$ mg

Table 5 shows the results found when this equations system was solved.

Sample	$CaCO_3$ (mg)	% $CaCO_3$
1	15.47	76.2
2	15.78	77.0
3	16.09	78.1
		Mean ± MSD: 77.1 ± 0.6

Table 5. Calcium carbonate content in three limestone samples.

• 4.2 MECHANISM OF DISSOLUTION OF CALCIUM CARBONATE BY ACID RAIN

As Figure 4 shows, the straight lines have a slop value nearly to 2, showing that in the reaction, two moles of bicarbonate ion are obtained by one mol of calcium ion, so, the proposed dissolution mechanism is the following:

$$CaCO_3 + 2\ H^+ \rightarrow Ca^{2+} + 2\ HCO_3^-$$

This mechanism is mentioned elsewhere like responsible of limestone dissolution (Leet and Judson, 1984). According this mechanism, acid rain is neutralized by calcium carbonate, and pH values of acid rain are incremented from 4.4 to pH values nearly to 8. At this pH values, the contribution due to bicarbonate concentration is very important when chemical balance of the solution is carried out.

5. CONCLUSIONS

Carbonate stones used in construction of Tajin and Maya monuments are being studied. It was shown that these materials are subject to chemical weathering processes by acid deposition.

It is imperative that governments take drastic steps to reduce the acid emission levels to the atmosphere, and only so, this mankind heritage will be able to be still admired in the future.

6. RECOMMENDATION

A Workshop proposal has been submitted to the National Science Foundation (USA) and the National Council for Science and Technology (Mexico), to take place if this proposal is approved in Merida, Mexico, at the end of this year. The Mesoamerican countries are expected to participate in this Workshop.

Acknowledgements

Authors wish to thank the following people for their effort to carried on this work: Dr. Yurgen Brugermann (died May 2004), responsible of restauration project of archeological zone at Tajin. Alejandro Santez, guard and responsible of sampling at Tajin.

Acknowledgements are also extended to Luis Javier Urbina Ramírez and Roberto Enrique Guerra García from the Center for Atmospheric Sciences.

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