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The Changes in the Structure of Limestone as a Result of Calcium Sulfate (Gypsum Stone) Formation Caused by Atmospheric Polluters

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Abstract: Limestone has been a frequently used building stone in many buildings and monuments throughout the history of civilization and it's still being used in today's buildings, especially the kind that's known as marble and it has a crucial importance among the natural building stones. Hovewer, when it is used as a building stone in the urban environments where the atmospheric polluters are dense, some negativeness could be faced due to the atmospheric polluters. Among these polluters, SO_x (sulphur oxides), NO_x (nitrogen oxides) and CO_x (carbon oxides) found intensly in urban atmosphere turns into an aggressive structure and causes serious damages on the limestone by merging with various factors acting as catalyst. The most important of these damage formations is the formation of calcium sulfate (gypsum stone) crust. Calciumsulfate develops on the surface of the limestone with the chemical reaction of atmospheric polluters and reachs a certain thickness and forms a thick crust layer in time. And in the next stage it disolves, tears in pieces because of the mechanic inner tension and the atmospheric factors such as rain, wind and frost and forthcoming damages and decompositions that can occur take a different dimension.

Key words: Atmospheric Polluters · Dry Deposition · Wet Deposition · Limestone · Calcium Sulfate (Gypsum Stone) · Stone Decay

INTRODUCTION

Pollutants that are known to have many harmful effect on living and nonliving things and that do not contain in normal composition of the air or even they are contained their ratio in the atmosphere increases (in solid, liquid and gas form), have significantly harmful effects both on monuments, a part of historical and cultural heritage and on the buildings we live in. For instance, as it is in the yellowing of 350 year old white marbles of famous Taj Mahal in India (Fig. 1) due to venting 70 tones of sulphur dioxide and carbonic acid from petroleum refinery that is 40 km away [1].

Detriment and degradation that occur on construction material show development as result of combination of pollutants with other atmospheric factors. It is not possible to claim that all of atmospheric factors such as rain, temperature, relative humidity, wind, sun light radiation, fog and air pressure have an effect on construction materials. The most important factors among them are rain, relative humidity, wind, sun light radiation and temperature [2].

Detriment and degradation that occur on construction materials do not cause rapid changes in the material and hence, they become visible only after a very long period (Fig. 2). Developments of detriments and degradations differ as of physical, chemical and mechanical properties of the construction material (Fig. 3). Natural stones contained in construction materials are construction materials that undergo the biggest harm from the effects of the pollutants and where detriment generation reaches to the most serious levels. The most important reason why natural stone construction materials are damages is related to the property and amount of carbonate in the structure of the stone. For instance, granite stones that do not have carbonate at all in their structure suffer significantly less damages from effect of air pollution such acids. However, in almost all types of

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Fig. 1: Taj Mahal, India (http:// www.tcetvelim.com/ muhtesem-yapilar/tac-mahal-aska-adanan-en-buyuk-yapi-video.html)

Fig. 2: Dissolution occured in sculpture on the Lincoln Cathedral (England). Upper photo was taken in 1910. In the lower photo, was taken after 74 years, in 1984 [3]

granites, there can be color changes, some grey colorful granites may turn into brown or yellow and even as result of degradation of iron particles inside granite, oxidization tarnishing can be observed on the surface [4]. Although some types of limestone that are often used in the structures enter into reaction with acids such as sulfuric or carbonic acids, some, on the other hand, show a great resistance even under very negative conditions.

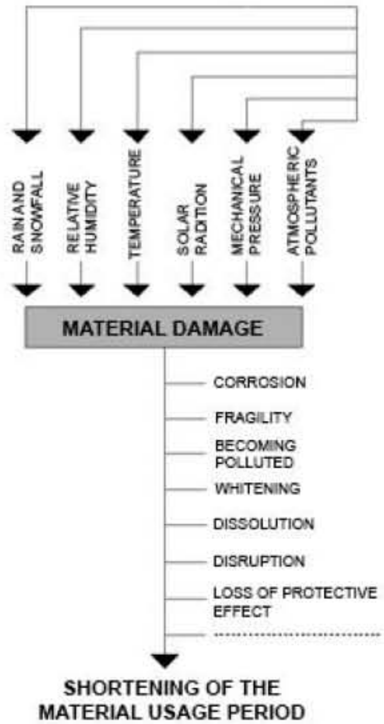

Fig. 3: Development of detriment and degradation as of physical, chemical and mechanical properties of construction materials [5]

While lime or clayey sandstone can even be effected from the pure rain water and can melt, types that contain silicate or iron are significantly resistant against acids or water.

Effect of Atmospheric Pollutants on Limestones: Detriment generation of pollutants such as SO_x (sulphur oxides) and NO_x (nitrogen oxides) that have first level importance and that are contained in atmospheric environment in very high rates, on limestones occur as result of the fact that pollutants reach to stone surface on two different ways:

“Dry Deposition Mechanism” that contains its gas form, “Wet Deposition Mechanism” that contains wet (acidic) form,

Primary pollutants that are found in almost all urban environments in relatively active and high ratios reach to stone surface in gas form with the effects of wind and turbulence in environments where rain or snowing does not occur and accumulate on the surface. In this event called as “Dry Deposition” [6], in reaching of atmospheric

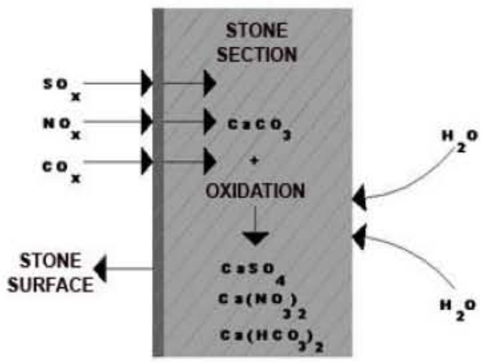

Fig. 4: Affection of atmospheric pollutants on limestone with dry deposition mechanism [8]

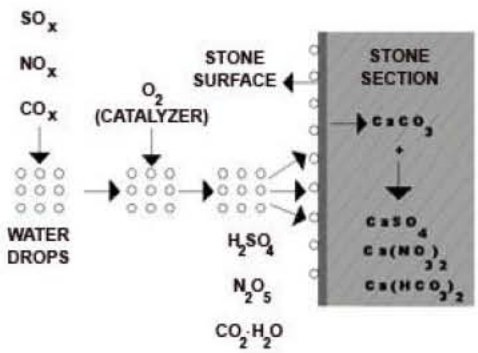

Fig. 5: Affection of atmospheric pollutants on limestone with wet deposition mechanism [8]

pollutants to stone surface in gas form (Fig. 4) and in the generation of detriment and degradation such as $CaSO_4$ (calcium sulfate/ gypsum stone), atmospheric factors such as the length of dry period, luminosity of sun light, wind velocity, dew, fog and relative humidity, catalysis such as O_2 (oxygen) and O_3 (ozone), characteristic properties of the stone, natural feature of the stone surface (roughness/slickness, porosity /porosity less), humidity and pH of the surface or stone structure, absorption ratio of the stone, status and amount of atmospheric pollutant concentration are highly important [7].

"Wet Deposition", a chemical composition that contains composition of dissolving of pollutants in gas form with water particles in rain water, atmospheric humidity (relative humidity), fog or clouds includes absolute concentration of pollutants in the air, location of pollutants in the atmosphere and particle sizes and their pH. According to this mechanism, H_2SO_4 (sulfuric acid) and N_2O_5 (nitric acid) that generate as result of conversion of pollutants such as SO_x and NO_x due to a chemical reaction starts the development of detriment and degradation within limestones by affecting on the stone surface as particles or by forming it on a surface where a very thin water layer resides (Fig. 5) [8]. And by turning the mechanisms of both dry deposition and wet depositions to $CaCO_3$ (calcium carbonate/limestone), $CaSO_4$ (calcium sulfate/gypsum stone) with the effect of different chemical reactions, thick gypsum stone crust occurs which is the most important development of these detriments and degradation stages on gypsum stones.

Alterations in Limestones with the Generation of Calcium Sulfate (Gypsum Stone): Developments and alteration in the generation of determined by the different chemical reactions of dry deposition and wet deposition of SO_2 (sulphur dioxide) can be defined mainly as the differences of thickness of gypsum stone occurring in lime stones, weight losses or increases, formation of black areas and surface erosions.

Differences in Thickness of Calcium Sulfate (Gypsum Stone) Crust: In the formation and development period of gypsum stone shelter observed over limestones, reaction ratios of $CaCO_3$ and SO_2 decreases of the reaction stages and the conversion of $CaCO_3$ to $CaSO_4$ changes depending on the time. Especially when marbles are damaged by SO_2 (sulfur dioxide) in the atmosphere, after a few hours after the interaction, conversion rate of $CaCO_3$, to $CaSO_3.1/2H_2O$ or $CaSO_3.2H_2O$ (calcium sulfite) decreases [9]. In the beginning, a very thing shelter is generated, but after this, gypsum stone shelter reaches to a certain thickness having developed rapidly. In an environment where the temperature is 20°C and relative humidity is approximately 88.3%, water particles are observed on stone surface and this water layer allows the process of a thicker gypsum stone crust generation in fixed steps. When the status of dolomites is compared with that of marbles, reaction rate on dolomites become continuous from the first moment and hence, a crust much thicker than the marble is generated in a few years; such that it can compose 40 μm. thick gypsum stone crust in dolomite that are under the concentration of SO_2 in 0.01-0.04 ppm. value between 9 and 38 years [10].

Changes in Limestone Depending on Calcium Sulfate (Gypsum Stone) Generation: Another important criterion in order to stage $CaSO_4$ development and to demonstrate the size its damages on limestone is the status of weight increases or weight losses depending on calcium sulfate.

Should the subject be analyzed in this respect, it is possible to say that weight increase in the reaction of dry deposition mechanism of SO_2 with gypsum stone and that weight loss occurs with the effect of wet deposition mechanism. For instance, when atmospheric environments is balanced with relative humidity of approximately 84% and when surface water accumulation does not occur, a certain amount of weight increase is observed in gypsum stone as result of chemical reaction of dry deposition mechanism of SO_2 and when there is surface water and catalyst O_3 reside in the environment, weight increase occurs much more [11].

Acid rain, a product of wet deposition mechanism, causes a significant weight loss in the gypsum stones. To explain it more explicitly, acid rain solution causes thawing in gypsum stones and it thaws, decomposes and removes both outer layer of $CaCO_3$ that composes original structure of the stone and $CaSO_4$ shell that concludes chemical reaction of H_2SO_4 from the surface.

The most important point that needs to be known regarding the dry deposition mechanism effects of sulfate dioxides causes weight increase in gypsum stone in the beginning with this mechanism and then stone surface, as result of direct or indirect contact of rain water, may suffer a mechanic damage caused by an inner tension in parallel with damage of a solution or characteristic structure of the stone and changing atmospheric conditions. And in the continuation of this event, although not much as effects of acid rain in wet deposition mechanism, there occur a certain amount of weight loss on limestones.

Development of Surface Erosions on Limestone and Calcium Sulfate (Gypsum Stone) and Effects of Rain Water: Surface erosions on $CaSO_4$ crust generated as result of reaction of lime stone and SO_2 with dry and wet deposition mechanisms show development in two different ways, namely “Dissolution Damage" and "Mechanic Damage". Dissolution damage often occurs as resuls of tensions in the internal structure of the stone depending on characteristic structure and sudden decrease and increases in rain water, temperature and relative humidity.

Dissolution Damage: Acid containing rain water that helps the generation of $CaSO_4$ by directly or indirectly affecting limestones at the same time plays an active role in breaking and dissolution of gypsum stone shell that becomes a glass layer by hardening. However, limestones that exhibits different behaviors according to their physical, chemical and mechanic properties may face a balance solution even in a clean atmosphere as result of effect of non-acid containing rain water. For example, solution rate occurred with the effect of rain water on the surface of a structure that is composed of limestones located in that kind of environment may change between 3 and 20 mm. in 1000 years [12].

In that kind of dissolution of limestones, dynamic order of rain water and raining rate have an important place. If rain water affect on surface as thin and plain layer, first water layer (film) is absorbed by the surface and then is chemically reactivated. When the rain is disorderly, chemically reactive solution on stone surface changes continuously and this causes thawing of stone even during heavy carriage [13].

Another factor that affect solution is the rate of rain fall. Especially, when rain fall is observed in low level, pH rate decreases as well in parallel to this and as contact period increases with stone surface, they become significantly effective in marble dissolution. In high rate of rain fall when a totally reverse case is experienced, pH rate increases rapidly and solution decreases [7].

The effect of non-acid containing rain water on gypsum stone implements in three stages and:

- Atmospheric gases such as SO_2, NO_x and CO_2 enter into reaction with rain water and conclude a chemically active solution,
- This solution converts limestone into $CaSO_4$,
- Solution rate of the stone increases more by this generated gypsum stone shell breaking in the next rain fall [12].

Solubility rate in lime stone changes subject to CO_2 concentration and acidity of the rain and when particles of 8 Ph reach 4-5 Ph, its kinetic solubility rate increases [13]. And as result of this, subject to form of gypsum stone shell and surface erosion generation, on stone surfaces: Small holes, deep or irregular abrasions with acid, cracks, deposition and falling are observed (Fig. 6). The fact that deep solution with acid occurs especially through crystal particle boundaries makes water affecting to deeper areas easier (Fig. 7) and causes increase in surface abrasion [14]. For example, in 1980-90s, in the measurements conducted in St. Paul's Cathedral (Fig. 8), it is found that a solution of 0.8 mm. on stone surfaces that were under the effect of acid-containing rain water for

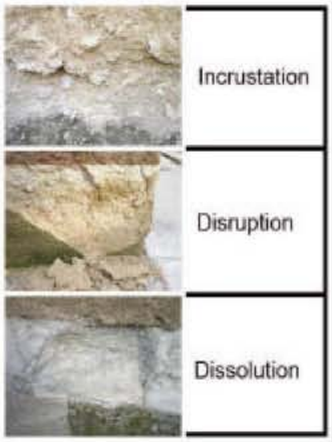

Fig. 6: Incrustation, disruption and dissolution on stone surface

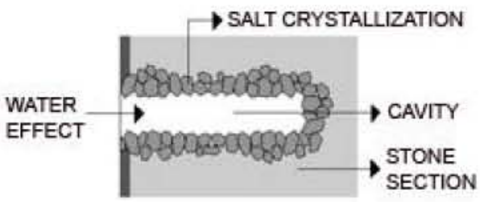

Fig. 7: Channel (hole) opening in limestone as result of deep solution with acid [18]

Fig. 8: St. Paul's Cathedral, England (http://www.answers.com/topic/st-paul-s-cathedral-large-image)

10 years and a solution of 0.3 mm. on surfaces protected from rain water effects [15]. For ancient marbles in Rome, on the other hand, this rate is between 0.15 and 0.25 mm in each century and between 0.03 and 0.05 mm in areas that are protected from outside effects [16]. In the examination in Norwich Cathedral (Fig. 9) constructed

Fig. 9: Norwich Cathedral, England (http://www.paradoxplace. com/ Photo % 2520 Pages/ UK/ Britain_Centre/Norwich_Cathedral)

Fig. 10: York Minster Cathedral, England (http://www.onlyrooms.com/en/destination/city/hotels-in-york/3991/1)

from oolitic limestone and in York Minster Cathedral (Fig. 10) constructed from limestones, solution rate was found much higher and surface erosion of average 3-4 mm. was measured for each century. Detection of approximately 30 mm. dissolution in parapets of St. Paul's Cathedral, in a period of 250 years [17] are important findings that demonstrated the size of dissolution damage that acid-containing rain water has formed.

Mechanic Damage: With mechanic damages occurring as result of main factors such as sudden decreases and increases in temperature and relative humidity, tensions occurring in the internal structure of the material depending on its physical, chemical and mechanic properties, freezing and melting of water, surface erosions that develop on gypsum stone on different forms are observed. Dry or wet deposition of SO_2, rain water that enters into chemical reaction, relative humidity or atmospheric fog, convert $CaCO_3$ into $CaSO_4$. In the next stage, temperature changes and other environmental changes in normal temperature causes squeezing and expanding of stone and as result of decossion of calcite crystals, mechanic damage occur with shrinking and breaking of stone pieces. Especially micro cracks that occur with thermal changes allow the acids located within atmospheric pollutants reach to deeper areas of the stone [19]. Or rain waters poured on the surface fills into these micro cracks and can fracture the stone by being frozen. Moreover, its breaking into pieces by undergoing crystallization pressure inside gypsum crust of dolomite stone with frequent and irregular changes of relative humidity can be classified as one of the different formation of mechanic damage [10].

CONCLUSION

Environment is the whole of values that creates the common value of the humanity and that are impossible to be conceded to survive. For this reason, life environments such as air, water and soil, plant and animal communities that share these life environments with humans and civilization that humans have created throughout history are all environmental values. The effects of atmospheric pollutants that have many known and unknown impacts on structure and monuments and present structures that reside in these environmental values, on natural stones used as construction material; on limestones and the change in gypsum stones as result of this effect are very clearly and explicit. Such that, separate or composite effects of chemical reactions of atmospheric pollutants defined as dry and wet deposition mechanism in very short time may cause significant material loss such as generation and development of $CASO_4$ (calcium sulfate/gypsum stone) crust on limestones. Generation of gypsum stone crust, atmospheric factors such as rain water and wind on the surface or within limestones used as construction material, surface abrasions and material losses, excessive temperature differences and mechanic internal tensions as result of freezing of water that fills into the cracks of the stone causes breaking and dispersing of stone.

As a result, formation of gypsum stone crust which one of the most dangerous formation to be observed in natural construction stones used as construction material often requires repair or renew of the stone that is damaged and given that these conditions are not fulfilled within time, problems whose solution are relatively difficult and that affects structure location and structure internal comfort negatively in the area that stone resides can develop. In this respect, generation of gypsum stone crusts formed over limestone as result of combination of various atmospheric factors and pollutants affects construction material and hence, use performance of the structure, negatively it is possible to consider it as an important factor that causes the generation of problems in structure damage and structure physics.

REFERENCES

1. Gökaltun, E., 2001. Atmosferik Kirleticilerin Kireçtaşları Mermerleri Üzerindeki Parlaklık Kaybına Etkisi (Published Doctoral Thesis). Anadolu University Publications, Eskişehir.
2. Simpson, J.W. and P.J. Horrobin, 1970. The Weathering and Performance of Building Materials. Medical and Technical Publishing Co. Ldt., Aylesburg.
3. Boşgelmez, A., 2000. Ekoloji 1. ISVAK Publication, Ankara.
4. Ragsdale, L.A. and E.A. Raynham, 1964. Building Materials Practice. Edward Arnold Ltd., London.
5. Anon, 1990. Atmospheric Pollution Effects. Environmental Engineering, 3(3): 27.
6. Lindberg, S.E., A.L. Page and S.A. Norton, 1989. Acidic Precipitation (Vol. 3). Edwards Brother Inc., Ann Arbor, Michigan.
7. Schuster, P.F., M.M. Reddy and S.I. Sherwood, 1994. Effects of Acid Rain and Sulphurdioxide on Marble Dissolution. Materials Selection and Design, 1: 78-79.
8. Amoroso, G.G. and V. Fassina, 1983. Stone Decay and Conservation. Elsevier Publishing, Amsterdam.
9. Gwin, J.A. and R.K. Popli, 1982. X-Ray Determination of SO_2-Marble Reaction-a Mathematical Model. 4th International Congress on the Deterioration and Preservation of Stone Objects, Lousville.
10. Tambe, S., K.L. Gaurl, S. Li and G. Cobourn, 1991. Kinetic Study of SO_2 Reaction with Dolomite. Environmental Science Technol., 25(12): 2075.
11. Johnson, J.B., S.J. Haneef, B.J. Hepburn, A.J. Hutchinson, G.E. Thompson and G.C. Wood, 1990. Laboratory Exposure Systems to Simulate Atmospheric Degradation of Building Stone under Dry and Wet Deposition Conditions. Atmospheric Environment, 24(10): 2996.

12. Lipfert, F.W., 1989. Atmospheric Damage to Calcareous Stones: Comparision and Reconciliation of Recent Experimental Findings. Atmospheric Environment, 23(2): 415.
13. Bresser, A.H.M. and W. Salomons, 1989. Acidic Precipitation (Vol.5). Edwards Brothers Inc., Ann Arbor, Michigan.
14. Viles, H.A., 1990. The Early Stages of Building Stone Decay in an Urban Environment. Atmospheric Environment, 24(1): 229.
15. Trudgill, S.T., H.A. Viles, R.U. Cooke, R.J. Inkpen, A.L. Heatwaite and J. Houston, 1991. Trends in Stone Weathering and Atmospheric Pollution at St. Paul's Cathedral. Atmospheric Environment, 25(12): 2582.
16. Guidobaldi, F. and A.M. Mecchi, 1993. Corrosion of Ancient Marble Monuments by Rain: Evaluation of Pre-Industrial Recession Rates by Laboratory Simulations. Atmospheric Environment (Part B: Urban Atmosphere), 278(3).
17. Feilden, B., 1994. Conservation of Historic Buildings. Butterworth and Co. (Publishers) Ltd., Chatham.
18. Haneef, S.J., J.B. Johnson, C. Dickinson, G.E. Thompson and G.C. Wood, 1992. Effects of Dry Deposition of NO_x and SO_2 Gaseous Pollutants on the Degradation of Calcareous Building Stones. Atmospheric Environment, 26(16): 2968-2969.
19. Fassina, V., 1988. The Stone Decay of the Main Portal of Saint Mark's Basilica in Relation to Natural Weathering Agents and to Air Pollution. 6th International Congress on Deterioration and Conservation at Stone, Torun.