THE IMPACT OF ENVIRONMENTAL CONDITIONS ON THE ROMAN TOMBS IN ALEXANDRIA CITY

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ABSTRACT

The Roman archaeological sites in Alexandria have built on oolitic limestone or excavated through it. They are suffering in particular in recent years from intensive weathering processes. The weathering features are noted as honeycomb, rock meal, rock surface disintegration and cracking. The weathering processes have been examined through the small stone samples collected from some archaeological sites e.g. Ras El-Tin, Kom El-Shokafa, El Shatbi and the Roman wall of Alexandria city. The techniques used for this are polished thin section study, scanning electron microscopic study to see the details of weathering on nano-scale. The results indicated that the main weathering processes are salt weathering in addition to the variation in climatic conditions.

Four resins namely have been examined to find which one and at which concentration can improve the hardness and the durability of the oolitic limestone that is easily weathered by such aggressive conditions. The results indicated that Rhodosil H 224 at a level of concentration 10% in white spirit gave the best results and highly improve the stone durability and increases stone resistance to simulated weathering processes done in the age accelerating chambers.

INTRODUCTION

As the roman archaeological sites in Alexandria city are valuable and have been damaged by weathering processes that are highly increased recently during the latest few decades, so this study aims to examine the weathering processes and intensity to find out how to conserve these sites from more damage to survive for many centuries. So, the work is focused on three locations as a case study where weathering is clear and they require urgent conservation. The study also is focused on examining four resins namely; Methylmethacrylate co-polymer, Rhodosil H 224 (polymethylsiloaxne), OH (Tetraethoexysilane), and H (ethyltrimethoxysilane) to be checked for consolidating the weathered stone surfaces of these archaeological sites. The bases of their evaluation are (1) Measuring their penetration depth within the stone, (2) Examining stone surface colour after using each resin, (3) Examining stone surface breathability after consolidation, (4) Examining stone durability after consolidation to find out which resin verify highest stone strength to weathering processes working in Alexandria as well as sites located on the Mediterranean Sea coast, and (5) Examining which resin verify better progress in the stone geotechnical properties.

FIELD STUDY:

The archaeological sites in Alexandria city have been visited and the weathering features were carefully noted and photographed at the selected areas. The field study included recording the weathering features and samples collection to be examined in the laboratory using the suitable techniques.

Honeycomb weathering is a common phenomena which affects monumental limestone in coastal environment, the processes involves the progressive development of closely spaced cavites or alveoli typically range from a few millimeters to several centimeters in diameter. Salt weathering play an important role in the deterioration of monumental limestone in Alexandria due to the salt crystalization in pores, crusts and efflorescences rich in halite, gypsum are the effect of marine spray and the effect of the attack of aerosol coming from the sea. Variations on humidity and temperatures around or inside the tombs play an important role in the crystalization – dissolution of different salts. The superficial deterioration of limestone in crust form and efflorescence consists of bicarbonates and sodium carbonate. The solutions in limestones take place initially as a result of mixing of rain water with carbon dioxide in the atmosphere which leads to cracking, splitting and flaking.

There is an increase in bicarbonate due to the dissolution by carbonic acid suggests that all weathering proceeds by chemical alternation of the limestone.

The presence of NaCl dissolution make the solubility of $CaCO_3$ increase. The sodium sulphate normally crystallizes in conditions of high relative humidity. At a temperature lower than 24° C and relative humidity higher than 75% of the $NaSO_4$ crystallizes (Arnold, 1989).

Finally the weathering forms in the study case are striations, undulating surfaces, fissures, splitting, flaking and finally stone loss. The weathering forms of the chemical deterioration affecting effloresence, scaling rill marks the most important feature of the differential weathering produce honeycomb. The honeycomb weathering in the study case resulted from the evaporation of sea water splash. Red and brown colors of the iron hydroxides are migrated and concentrated in the cracks of the Roman wall. Also, a deposits of calcium carbonate, sodium chloride and gypsum precipitate along the cracks. The green colors which are mainly located at the lower parts of the Roman walls and the tombs sites resulted from effects bacteria, algae and fungi.

The most dominant weathering features at the areas under investigation as well as at many other locations on the Mediterranean Sea cost are stone surface discoloration with a white salt efflorescence and green colour algae (Fig. 1), rock meal which is alteration of the hard rock surface into powder due to weathering (Fig. 2), and severe honeycomb and stone surface scalling (Fig. 3,4). Such later form weathering is highly diagnostic for salt weathering as recorded before by many authors (Gill, 1981, McGreevy and Smith, 1982, Wellman and Moses, 1996).

Stone samples have been collected from the weathered parts to examined in detail using thin section and scanning electron microscope.

Water samples have been also collected from the sea and domestic water at locations of study to find out their salt content and to be compared with that of the construction rock of these sites. This is to find out the salt source to these sites through the hydrochemical analyses for these water samples and the extracted solutions prepared from the stone samples following the method of Rhoades (1982).

LABORATORY RESULTS AND DISCUSSION:

This research has two divisions of laboratory results; the first one is for examining weathering processes acting on the archaeological sites at the selected areas using the following techniques: polished thin sections, Scanning Electron Microscopic study as well as hydrochemical analyses. The second division in this work is to examine and evaluate the four resins selected as stone surface consolidating material for the weathered stone surface following the five bases mentioned above.

The following is the laboratory results for the weathering processes.

Petrographical study:

Thin sections have been prepared from the stone samples collected from the sites under investigation to examine their texture type and stability of its mineralogical composition. Folk (1959) and Dunham (1959 and 1962) classifications of the limestone texture have been used to give an accurate type of the limestone composing these sites. The limestone texture type is found to be two types namely; Sparitic packstone type (Fig. 5) that is allochems cemented by sparry calcite and the allochems lost most of its internal mirotexture due to micritization by endolithic algae. Such facies type has low porosity due to filling rock pores by sparry calcite, and such facies type has recorded before to be easily weathered by salts more than micritic limestone (Kamh, 1994 and 2000). The second facies type is porous packstone (Fig. 6) where allochems are packed together but the cement is mostly lost and the rest is isopachous microspar and this type have got two types of porosity, both can be noted on (Fig. 6) Such thin section study through light on how much weathering could be easy on such weak texture of this limestone and that porosity is enough to enhance the weathering impact deeply within the stone.

Scanning electron microscopic study:

It has been done to give more details about stones weathering on nanoscale. It revealed that the stone composing the archaeological sites under investigation has different forms of weathering noted as grain surface damage and micro-exfoliation (Fig. 7). The scanning study also enables us to see the salt content in the collected rock samples, Halite salt can be seen in two phases of crystallization they are cubic form (Fig. 8) and whiskers form (Fig. 9). The second form is highly serious as it has high surface energy that can destory rock texture (Gauri, 1990).

The salts from efflorescence and crust are composed of crystals well visible under a microscope (Figs.10,11). Sodium chloride reflect the specific crystal form e.g. whose familiar form are nice cubes as visible in (Fig.12) may form very long prisms and hair – like crystals as in (Fig.11) or of loose aggregates of whiskers forming fluffy efflorescences (Fig.14). Traces of crystalline salts mixed with crypto – crystals accumalted in the bottom of free ooides (Figs.12,14). Other crystalline salts deposited on the surface of calcite crystals and space among. SEM shows the disintegration of calcite crystals due to the effect of soluble salts (Fig.12,13). The ooides of limestone and it rounded form were completely deteriorated bby the attack of soluble sulphates and chlorides. (Fig.15) shows the amount of sodium chloride increased with depth whereas the sulphates remained on the surface due to the differential mobility of salts in the solution linked to their solubility. Also, it should be noted that the content of gypsum in the samples is due to the transformation of calcite into gypsum. There is a reciprocal correlation between decrease of carbon content and increase neo – formed gypsum as observed on the investigated samples under scanning electron microscope. The gypsum take place at first in calcite by partial or total substitution of the carbonates. Further it proceedes by substituting some elements of stone matrial. SEM shows the dissolution of the internal microtexture of the limestone. This fact leads to an increase in porosity and loss of cohesion of the stone. EDX analysis show high content of chlorine as in (Fig.16) due to the salt crystallization of halite in the pores of limestone. (Fig.17) shows a big loss of Ca due to the carbonic dissolution of limestone in marine environment and there is an increase in the dissolved bicarbonate with high content of Na^+, Cl^- from halite and sulpher (S^-) from sulphates.

From this study it can be noted that salt weathering is the main reason of stone surface damage at study area. Thus, hydrochemical analyses has been done on the water samples collected from the sea and domestic water as well as on extracted solutions prepared from the collected stone samples.

Table (1) Hydrochemical results of the water and stone samples at study area.

Sample type	E.C. (mmhos/cm)	T.D.S. (PPm)	NaCl%	KCl%	$NaSO_4$%	$CaSO_4$%
Sea water	26.3	30.2	11250	54.2	6.8	12.7
Domestic water	46.7	26.8	10950	29.9	9.1	14.3
Stone sample(1)	17.5	33.7	121750	60.9	10.1	11.5
Stone sample(2)	23.0	35.1	142211	58.2	9.8	9.0

From the above results, it can be concluded that the construction stone of these sites has high concentration of salts that are mainly coming from sea spray and partly from domestic water as these areas are closely bounded by recent and old multi-storeys. The salt content of the extracted solutions of these stone samples is several times as that of the seawater due to continuous salt supply to stone surface, then drying by wind and insolation heating for several cycles results in high salt concentration at and on stone surface as indicated from the SEM and the hydrochemical analyses. The impact of these salts is very high where the net result of weathering as noted from the field observations is severe damage to these sites.

The Alexandria limestone is characterised by porous back stone texture with high porosity and made up of a large quantity of ooides and micropores. This characteristic gives the stone a high capillary absorption rate, and its consequent ability to absorb water and this is the main cause of decay, which manifests itself in the form of “honeycombing” (Figs.13,15). This phenomena affects nearly all of limestone in Alexandria which therefore requires a kind of suitable protective treatment.

The four resins under investigation have been prepared and used as stone surface consolidants for this weathered oolitic limestone after cleaning the samples from loosen particles. The samples have been put for evacuation first before soaking in each resin, then immersion of these samples have been done in this evacuation conditions.

Artificial weathering

The following experimental conditions used for the purpose of artificial weathering aimed at simulating as well as possible of the actual causes of environmental deterioration to quantify the durability of the treatments.

1) Wet – dry cycles

The test was applied to samples measuring 5×5×5 cm (3 samples per treatment, compared against 3 untreated samples) consisting of cyclic immersion and drying as ffollows:

- 16 hours total immersion in distelled water.
- 8 hours in an oven at 60° C.

A total of 30 cycles were carried out.

At the end of the weathering cycles, the material was tested for its water absorption by capillarity for fixed period. The results are shown in (Fig.25).

2) Salt crystallization weathering:

The test was carried out on samples measuring 5×5×5 cm (3 samples per treatment, compared against 3 untreated samples) the samples were subjected to cycles as follows:

- 4 hours of total immersion in a saturated solution of sodium sulphate.
- 28 hours of exposure to air in normal room conditions.
- 16 hours in an oven at 60° C.

The effects of the testing were monitored visually on each sample and periodical weight readings were also taken. The results are shown in (Fig.26).

3) Acid fog weathering

the test was carried out on samples measuring 5×5×5 cm (3 samples per treatment, compared against 3 untreated samples) were subjected to an acid fog of H_2SO_4. Cyclic tests were carried out as follows:

- 2 hours of exposure to acid fog.
- 10 hours exposure to an IR lamp.
- 17 hours in environmental conditions.

40 cycles were carried out using H_2SO_4 (3%), further 20 cycles using H_2SO_4 (5%) were carried out. Capillary water absorption at fixed period readings were taken 10 cycles and weight readings were also taken. The results are shown in (Fig.27).

The follwing is a results and discussion of the second division of this work to get the aim of study.

The four resins can be arranged in an order of decreasing quality as follows:

Rhodosil H 224. It verified the greatest penetration depth (3 cm within the stone), and its form at the maximum zone of penetration can be seen on the SEM photomicrograph (Fig.18), it does not change stone surface colour, and it keeps rock beathability, and it improved the geotechnical properties of this rock where its porosity is reduced by 80% of its original, its bulk density increased by 29% of the original. After artificial weathering the porosity is reduced by 79% of its original, its bulk density is increased by 26.5 of the original and its durability to salts is highly increased and reached up to 59% of the original as in (Figs. 22-25)

H (ethyltrimethoxisilane): It verified a considerable penetration depth (2.1 cm within the stone), and its form at the maximum zone of penetration can be seen on the SEM photomicrograph (Fig. 19), it does not change stone surface colour, and it keeps rock beathability, and it improved the geotechnical properties of this rock where its porosity is reduced by 73% of its original, its bulk density is increased by 22.6% of the original and its durability to salts is highly increased and reached up to 50.1% of the original. After artificial weathering the porosity is reduced by 72.3% of its original, its bulk density is increased by 20.9% of its original and its durability to salts is increased and reached up to 39.2% of the original as in (Figs.22-25).

Methylmethacrylate Co-polymer: It verified a considerable penetration depth (1.05cm within the stone), and its form at the maximum zone of penetration can be seen on the SEM photomicrograph (Fig.20), it does not change stone surface colour, and it keeps rock beathability, and it improved the geotechnical properties of this rock where its porosity is reduced by 25.4% of its original, its bulk density is increased by 15.9% of the original. After artificial weathering the porosity is reduced by 23.6% of its original, its bulk density is increased by 13.6% of its original and its durability to salts is highly increased and reached up to 15.9% of the original as in (Figs. 22-25).

OH (Tetraethxysilane): It verified a considerable penetration depth (0.09 cm within the stone), and its form at the maximum zone of penetration can be seen on the SEM photomicrograph (Fig. 21), it does not change stone surface colour, and it nearly keeps some what the rock beathability, and it improved the geotechnical properties of this rock where its porosity is reduced by 15.0% of its original, its bulk density is increased by 10.9% of the original (Figs.22-25) After artificial weathering the porosity is reduced by 14.2% of its original, its bulk density is increased by 9.3% of its original and its durability to salts is highly increased and reached up to 10.2% of the original. But this resin is just surfacial so when the surfacial consolidated part is removed on weathering then the weathering rate will be as before consolidation.

Overall, the results obtained by means of the various experimental tests are listed in table (2,3) and provide the following observations:

Water absorption by capillarity: excellent data from polymethylsiloxane ethyltrimethoxsilane performance is good. Methylmethacrylate and tetraethoxysilane offers poor performance.

Water absorption by total immersion: Excellent results from polymethyl- siloxane and good results with ethyltrimethoxsilane while tertaethoxysilane offers poor results.

Salt crystalization weathering: excellent results from polymethysiloxane followed by ethyltrimethoxsilane, and then methylmethacrylate followed by tetraethoxysilane.

Acid fog weathering: Rhodosil H 224 resist well with a reduced water repellence. Trimethathoxysilane also perform well though show a reduced water repellence than the above product. Methylmethacrylate and tertaethoxysilane offers low level of resistance than the above product.

So, for stone surface consolidation, the resin is suggested to get the best consolidation and water repellence. This product Rhodosil H 224 proves to be the most appropriate for the protection of Alexandria limestone.

CONCLUSION

The roman structures in Alexandria city as well as on the coast of the Mediterranean sea suffer from sever weathering by salts derived by sea spray and domestic water. These salts crystallize within rock texture and destroy it to different degrees.

In the case investigated here, marine salt weathering mainly involves(1) chemical alteration at the surface of limestone.(2) chemically leaching of calcite in the stone.

The porosity characteristic of the oolitic limestone which facilite the ingress and retention of saline fluids. The high reactivity of limestone materials with respect to salt from the Mediterranean sea as a supply of salt bearing fluid accelrates the salt weathering and the decay of stone which leads to the development of closely spaced cavities in initially solid stone.

The investigation of samples show that the crystalline chlorides exert a pressure on the pores of stone which cause spalling and cracking of the stone.

SEM studies show that the crystalline sulphates increase in the volume, therfore stress are created on the pores of stone, causing cracks in the internal structure of the stone.

Also, chlorides can penetrate to greater depth inside the stone. These crystalline salts disintegrate the limestone and change it into a brittle mass.

Consolidating material (Rhodosil H 224) has been carefully selected to not react passively with the stone under consideration and gave the best results in terms of the bases of resins evaluation. It is recommended for consolidation in Alexandria and for similar places with such stone type and stone weathering features.

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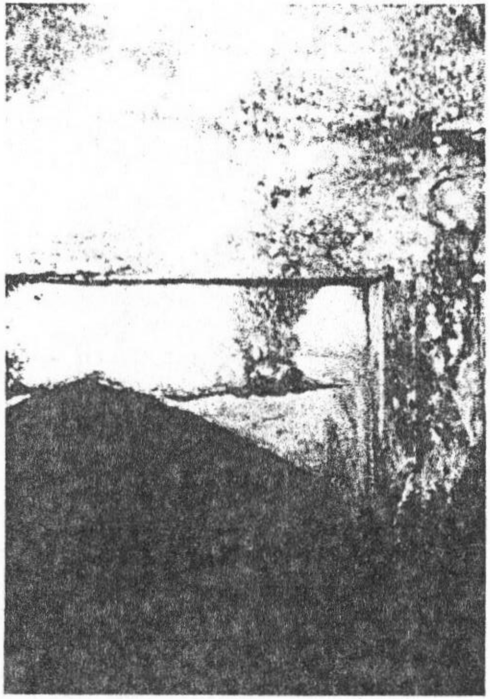

Fig.(1) Stone surface discoloration and green colour algae.

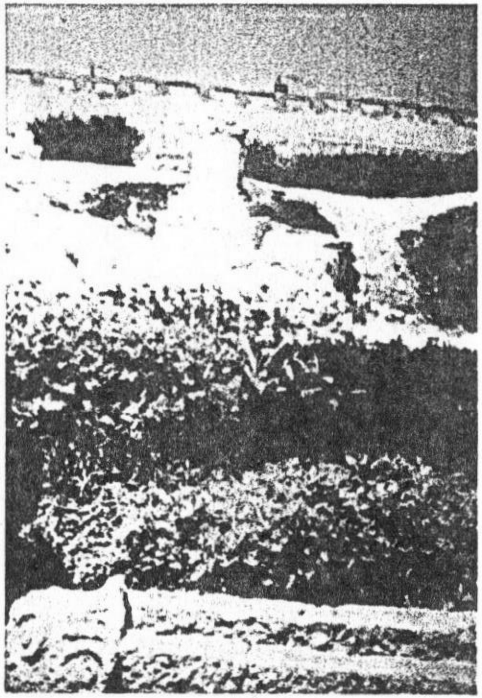

Fig. (2) Alternation of rocks to rock meal and intensive stone damage.

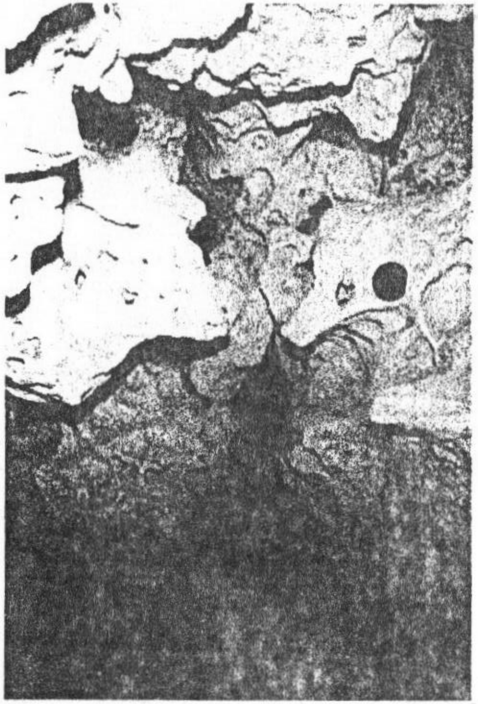

Fig.(3) Stone surface scalling and intense honeycomb.

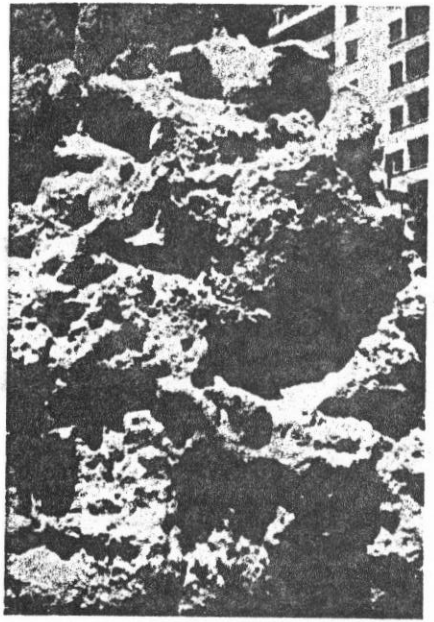

Fig. (4) Severe honeycomb on stone at study area.

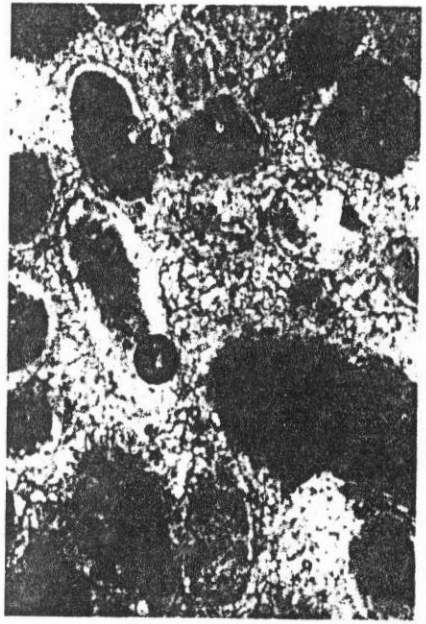

Fig.(5) Thin section photomicrograph showing sparitic packstone texture.

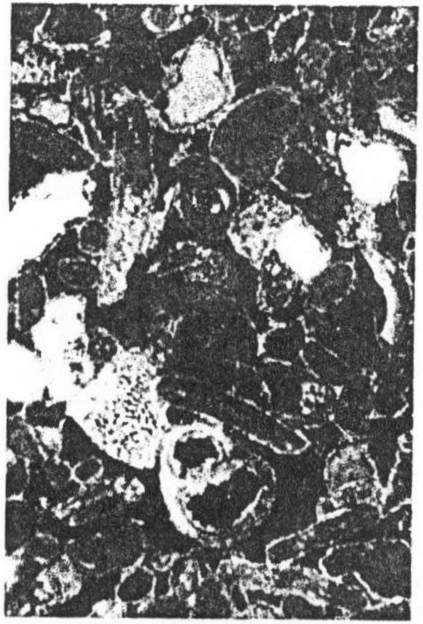

Fig.(6) Thin section photomicrograph showing porous packstone texture with isopachous microspar.

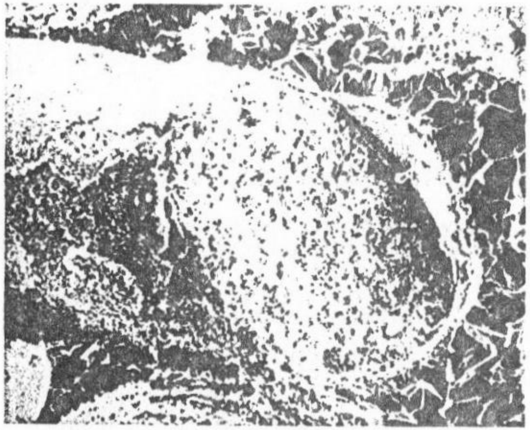

Fig.(7) Scanning electron phtomicrograph showing details on sparitic cement in the oolitic limestone.

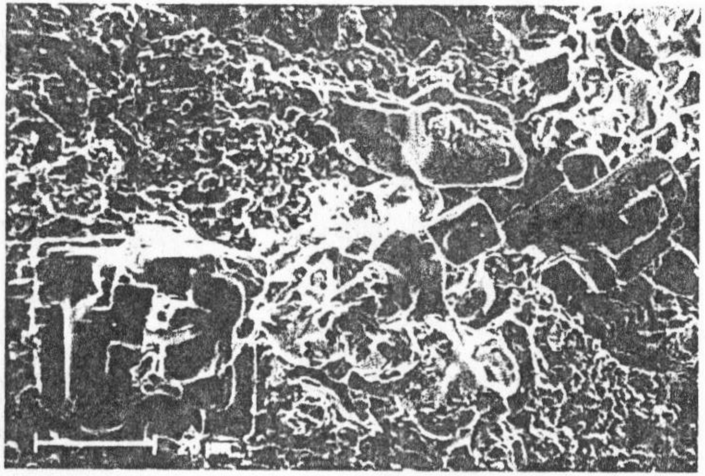

Fig. (8) Scanning electron photomicrograph showing Halite salt crystallize in the cubic form in the examined limestone and disfigring of calcite crystals.

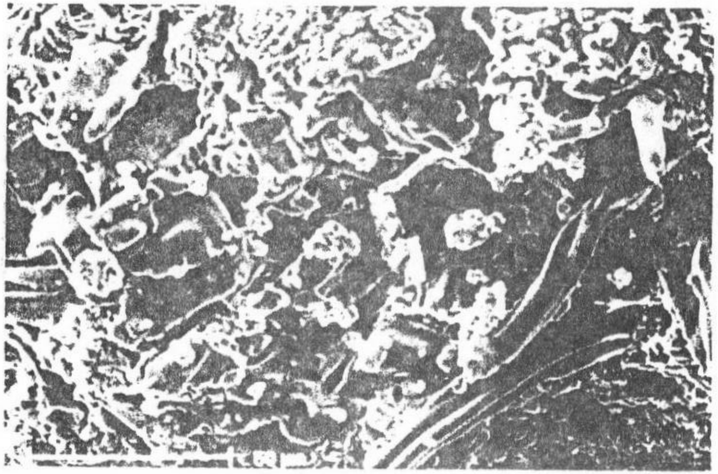

Fig.(9) Scanning electron photomicrograph showing Halite salt crystallize in the form of whiskers in the texture of the examined limestone.

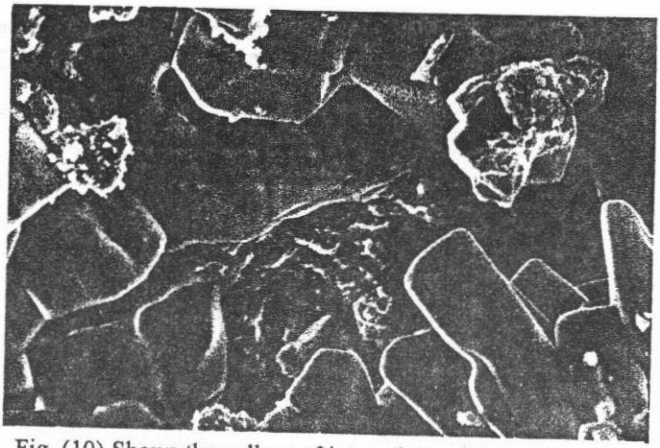

Fig. (10) Shows the collaps of internal stracture of limestone and the crystallization of gypsum.

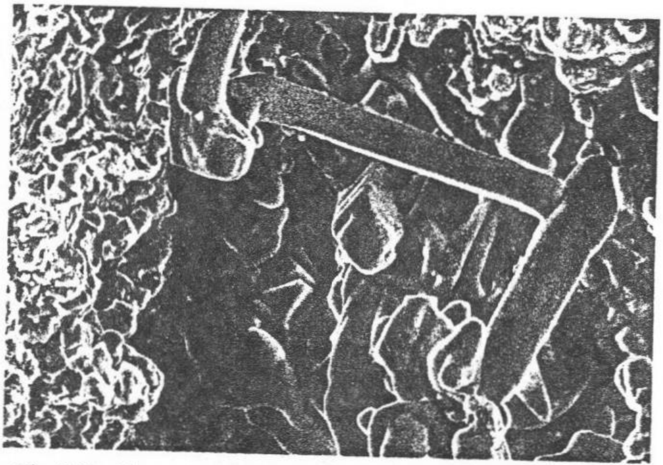

Fig.(11) Shows a well crystalization of salts and the distentegration of calcite.

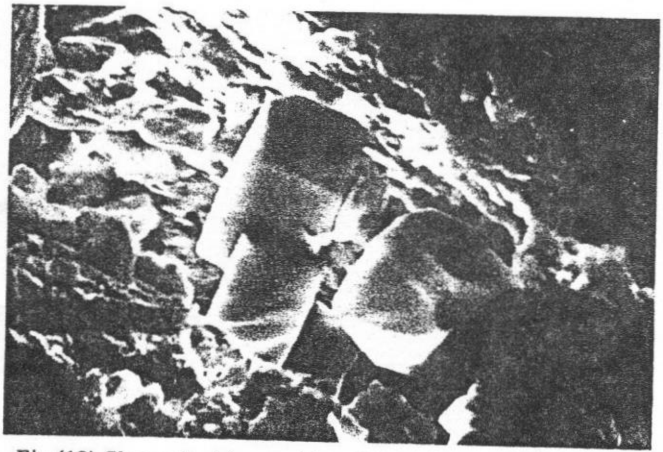

Fig.(12) Shows the idomorphic cubic crystals of Halite.

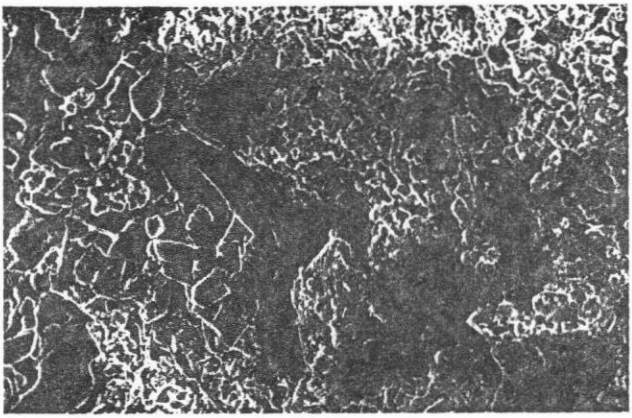

Fig.(13) Shows the dissolution of the internal microstructure of calcite.

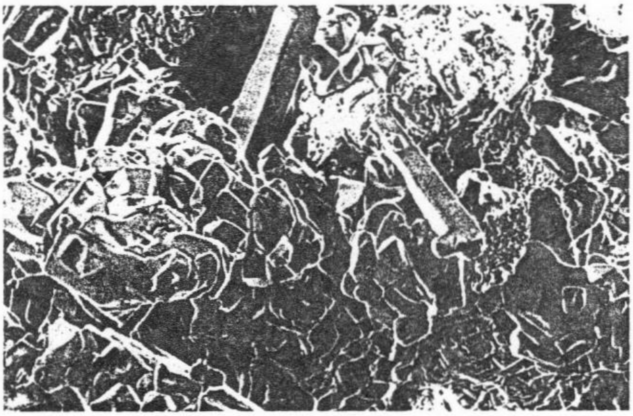

Fig.(14) Shows cluster gypsum crystals and the crystallization of Halite in the form of long prisms and hair-like crystal.

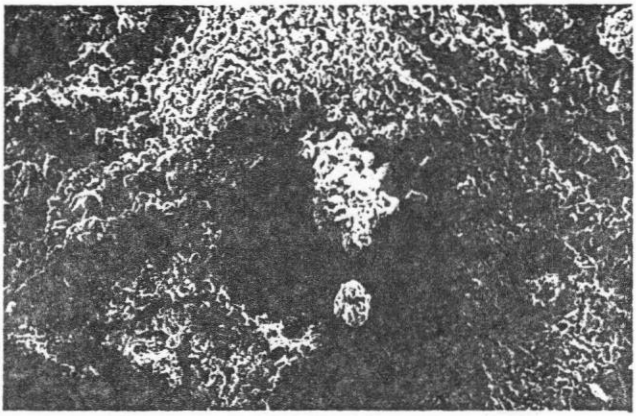

Fig.(15) Shows the crystalline chloride and sulphates exert a pressure on the pore stone which cause spalling and the stone cracking of the stone and the disintegration of stone.

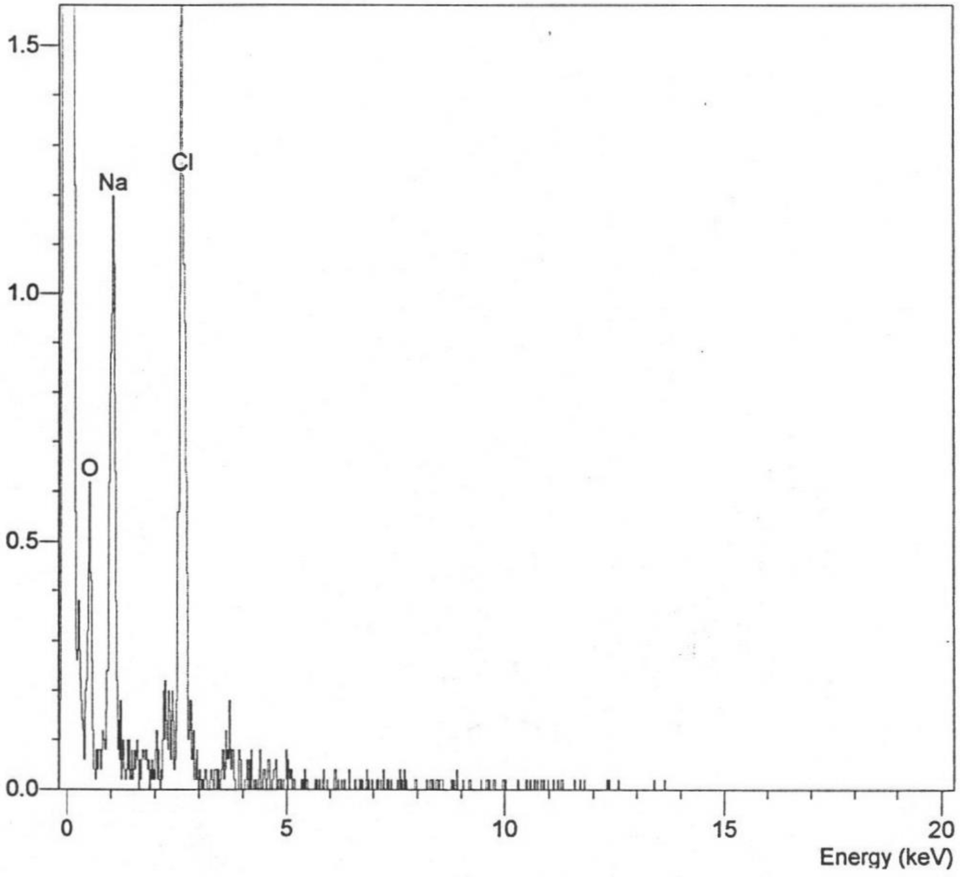

Fig.(16) Shows high content of sodium and chlorine due to salt crystalization of Halite.

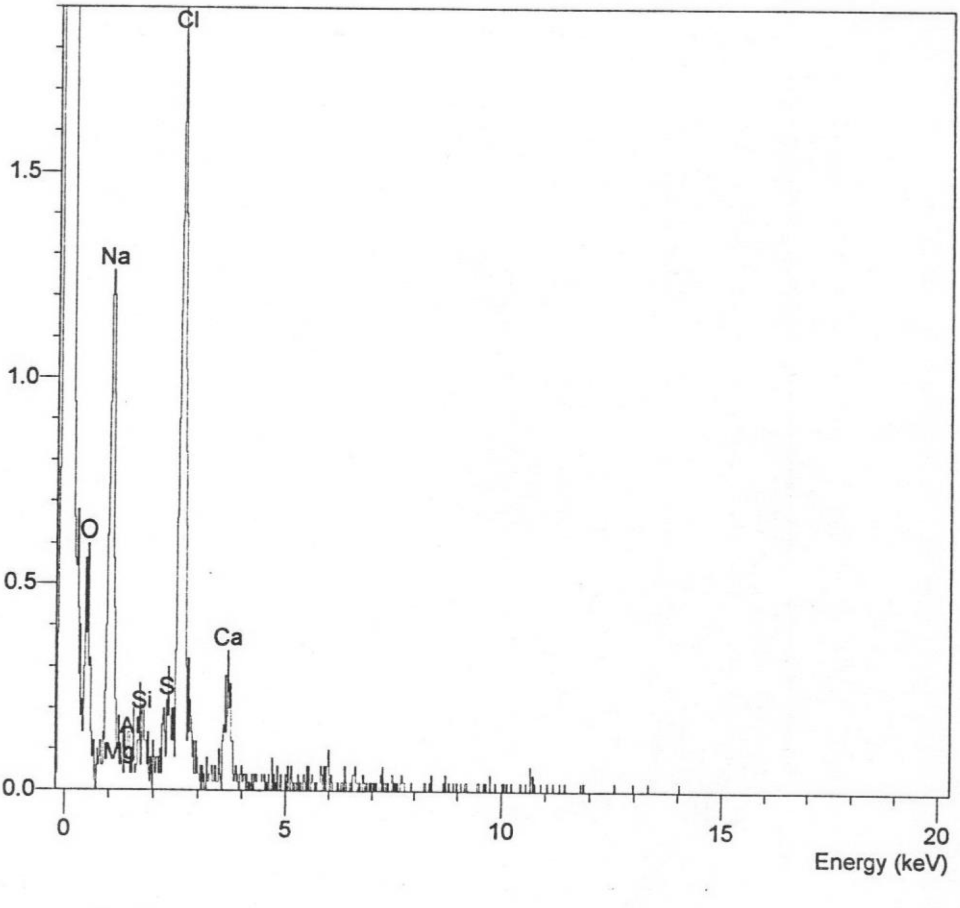

Fig.(17) Shows the loss of Ca due to the dissolution of calcite with high content of Na, Cl from halite and suluphur (s) from sulphates.

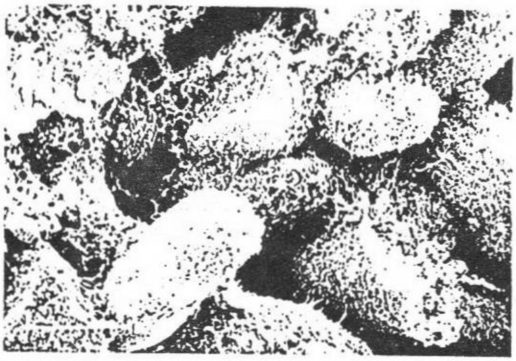

Fig. (18) Scanning electron photomicrograph showing the form of the resin with best penetration depth.

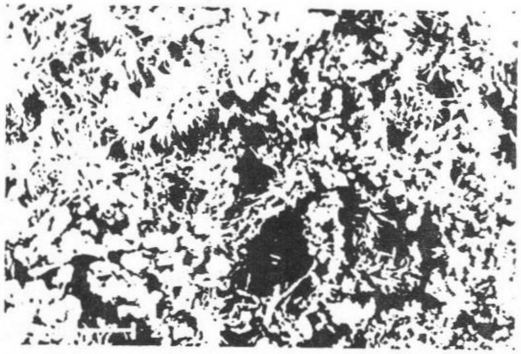

Fig. (19) Scanning electron photomicrograph showing the resin needle form.

Fig. (20) Scanning electron photomicrograph showing the resin with spider form.

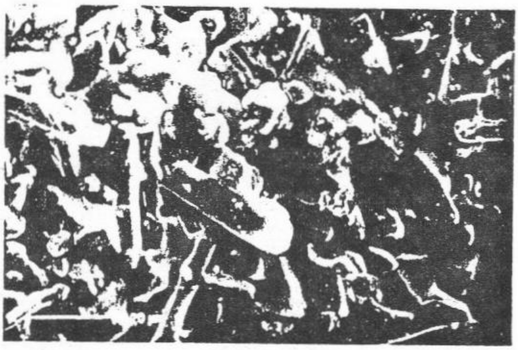

Fig. (21) Scanning electron photomicrograph showing the resin as thick gel killing rock breathability.

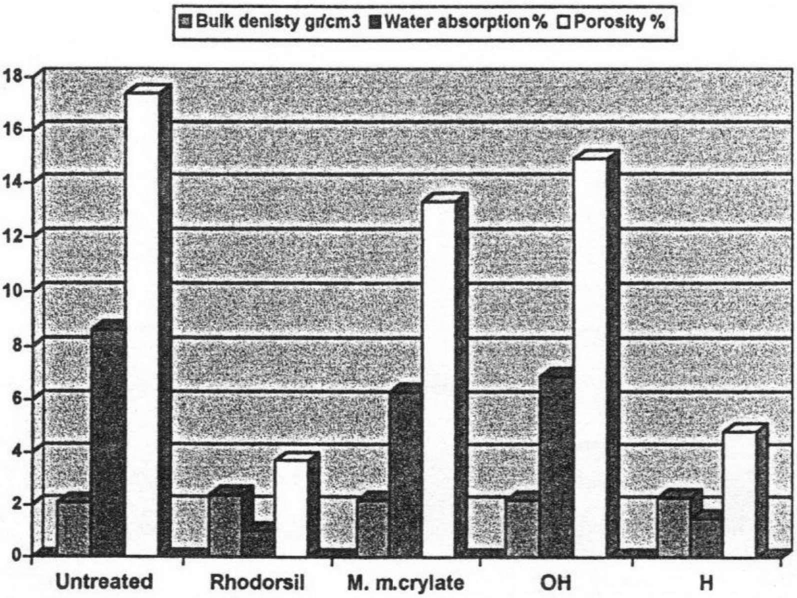

Fig.(22) Shows the physical properties before and after treatments by differents products.

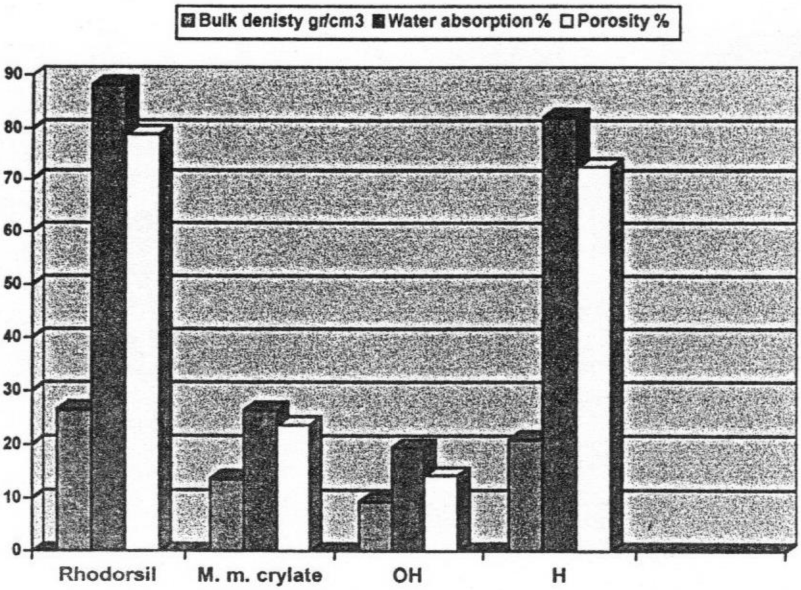

Fig.(23) Shows the percentage of changes in the physical properties before and after treatments by differents products.

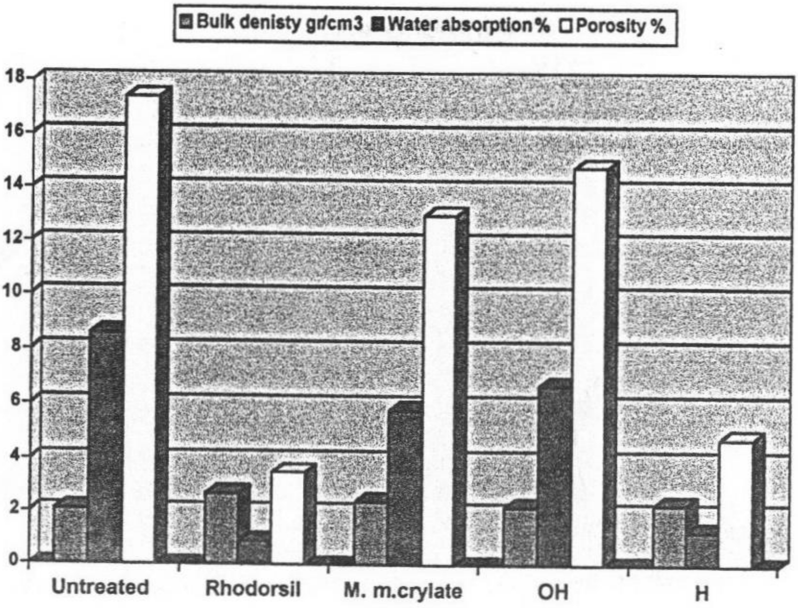

Fig.(24) Shows the physical properties before and after artificial weathering.

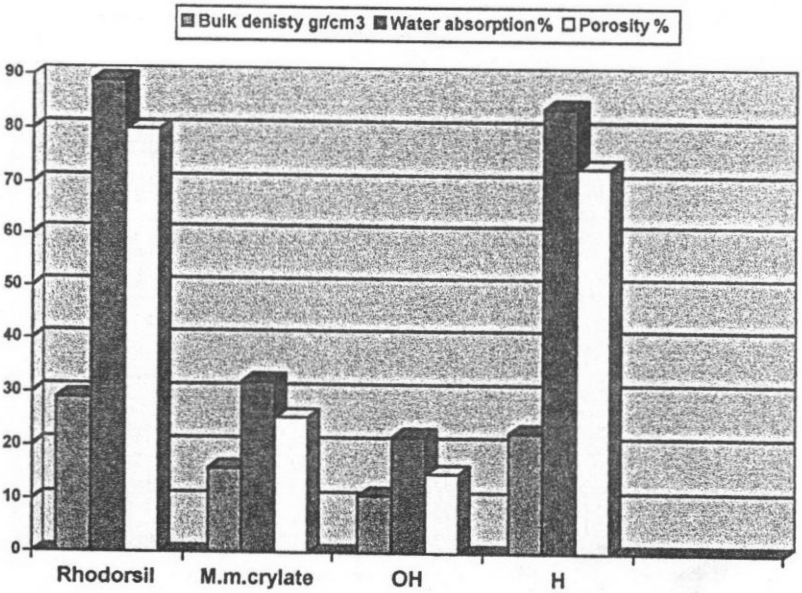

Fig.(25) Shows the percentage of changes in the physical properties before and after artificial weathering.

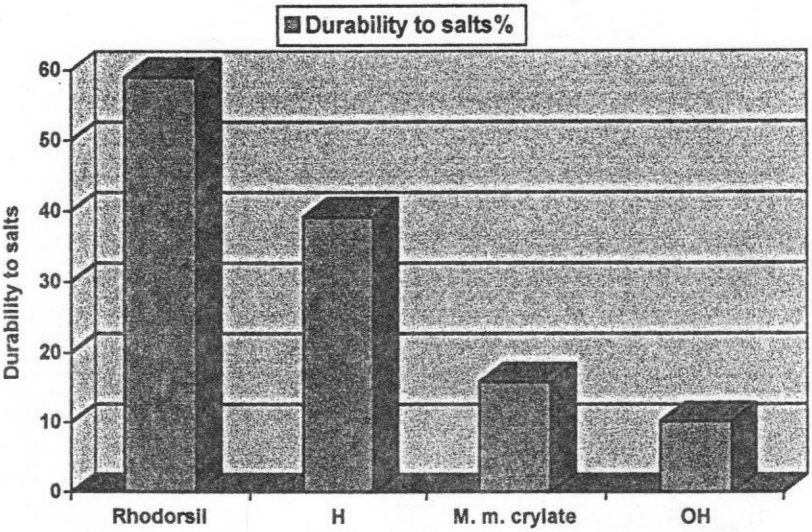

Fig.(26) Shows the percentage of weight loss before and after treatment in condition of salt weathering.

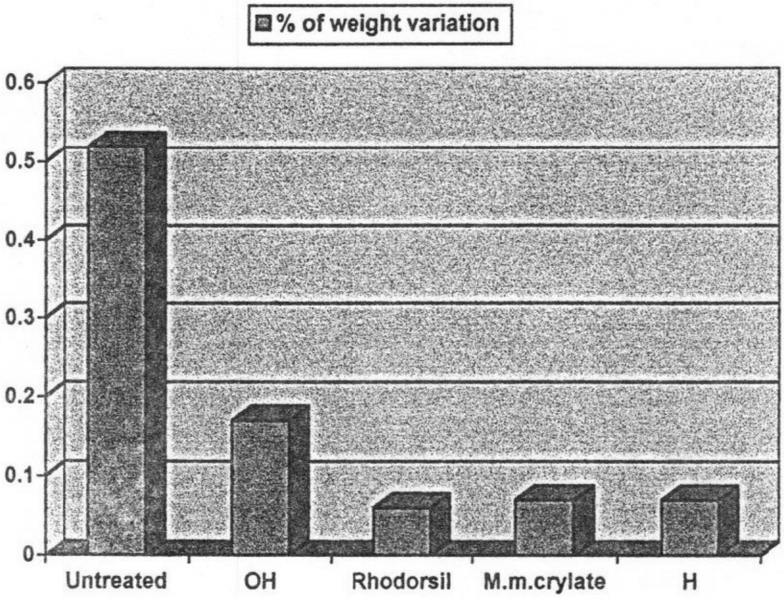

Fig.(27) Shows the percentage of weight variation before and after treatment in condition of acidic fog.