STUDIES OF SOME PHYSICO-CHEMICAL & BIOLOGICAL ASPECTS OF BUILDING STONE DETERIORATION & PRESERVATION

THESIS

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By

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Dedicated

to

Grandfather

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **STUDIES OF SOME PHYSICO-CHEMICAL AND BIOLOGICAL ASPECTS OF BUILDING STONE DETERIORATION AND PRESERVATION** in fulfilment of the requirement for the award of the Degree of Doctor of Philosophy, submitted in the Department of BIOSCIENCES AND BIOTECHNOLOGY of the University is an authentic record of my own work carried out during a period from January 1983 to December 1987 under the supervision of Dr.C.B.Sharma and Dr.G.S.Mehrotra.

The matter embodied in this thesis has not been submitted by me for the award of any other Degree.

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This is to certify that the above statement made by the candidate is correct to the best of our knowledge

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(GUIDE) **(GUIDE)** **(EXTERNAL EXAMINER)**

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ABSTRACT

Stone is considered to be the most durable building material but its durability is not absolute. Stone deterioration is attributed to a number of physical, chemical and biological factors along with environmental factors. The unfavourable environmental conditions result in the complicated process of chemical deterioration and physical disintegration of stone. The biological factors are closely interrelated with physico-chemical factors.

The present study embodies the physical, chemical and biological factors responsible for the decay of building stones. The samples of stones, used in the construction of historical monuments of India, namely Makrana marble, red sandstone, white spotted sandstone, basalt and scoria, were collected from monuments as well as from the respective quarries for a detailed investigation of their decay and durability characteristics under different environmental conditions.

The biological studies were made to identify the micro-organisms resposible for the deterioration of building stones. Microbial samples collected from a variety of monuments of Delhi region showed the wide occurence of algal and bryophyte growth over the rough and disintegrated stone surfaces. Among algae, the species of Cyanophyceae and among bryophytes, Riccia and Funaria were found abundantly. Altogether seventeen species of Cyanophyceae algae could be identified. The deve-

lopment of microbial population over the stone surfaces can cause morphological, mechanical and chemical changes in the stones which further enhance the decay of stones. The application of preservatives have been found effective to retard the growth of microbial population over the stone surfaces.

The physico-chemical studies of different stones have been carried out by durability test, weathering test, sea-water test and acid test. The durability studies have clearly revealed that the decaying behaviour of each variety of stone has direct relation with the physical characteristics e.g. water absorption and porosity. The general trend found in most cases is the progressive increase of these characteristics with the decay of stone. Further, the stone starts to disintegrate when it attains certain fixed values of water absorption and porosity depending upon the inherent characteristics and nature of the stone. Based on the above relationship established between the physical properties and decaying behaviour of each variety of stone, one can easily assess the remaining life of the particular stone used in the monuments and suggest the need for the preservation.

The pattern of disintegration of stone has been found to depend on its texture and structure. In Makrana marble the disintegration starts with the surface roughness and corner disintegration followed by development of irregular micro-cracks, while in sandstones, the disintegration starts with surface roughness and development of cracks along the bedding plane which become more prominent with the decay of stones resulting into separation along the bedding plane. In basalt the leaching of weathered secondary minerals from the amygdals promotes the development of grooves and pits over the surface-rich in brownish alteration material leading to irregular cracks over the surface. The scoria samples showed the decaying pattern in the form of high degree of surface erosion causing damage to corners and resulting into heavy loss in weight.

The durability and weathering characteristics of un-treated scoria stone was found to be different from other stones which may be due to highly porous structure of the stone.

Among the various preservatives, e.g. barium hydroxide, polymethylmethacrylate, styrene and silicone resin applied on the stones and studied for their decay and durability charac-teristics, the silicone resin has been found most effective preservative for the conservation of these stones. It forms a strong adhesion bond with the stone material and also preserves the original colour, structure and texture of the stones.

CHAPTER I

INTRODUCTION

CHAPTER I

INTRODUCTION

''An important part of our culture is chiseled in stone, and we are in danger of losing it ''.

Natural stone, is undoubtedly the oldest building material and has been in extensive use since the dawn of civilization. The most authentic records of the history, customs, and ideas of our ancient cultures are found chiseled in the stone. Stone has always been regarded a material of 'par-excellence' in its ornamental and aesthetic effects. Stone is still preferred by architects and property owners because in addition to imparting beauty to the structures it combines high strength and durability.

It is difficult to trace the exact history of ancient works on Indian building stones with any precision mainly because little attention was paid towards this aspect. For the first time in 1832, Hardie described the stones of Rajasthan. Later, Middleton (1869) and Cowasjee (1871) worked on building stones of certain areas. Meddicott (1874) and King (1890) described the distribution of building and ornamental stones of India. Sills (1875) published a note on the subject and reported certain engineering aspects of the building stones.

The selection of stone as a durable material by observation of its behaviour and condition in old buildings or other exposures, was first stressed by Vitruvius (1880). Hirschwald (1912) devoted life time to the study of testing of building stones. Many of the present test methods are based upon his work. Anderson (1911), Lucus (1915), Merrill (1921), Fox (1925), Laurie (1925), Turner (1926) and Baines (1927) carried out extensive studies on the weathering and durability of natural building stones. Later on, considerable studies have been carried out by Building Research Station (BRS) (1939, 1950, 1959, 1975), Schaffer (1950, 1951, 1955, 1966, 1967) and Winkler (1973). All these authors highlighted the characteristics of the building stones which cause their undesirable behaviour. They emphasized the need for thorough examination of the stones especially durability and weathering characteristics in the environment where the stones are to be used for construction of buildings or monuments.

1.1 CAUSES OF DECAY OF STONES

In India most of the historical buildings and monuments are made of stones which have withstood the ravages of the weather for centuries. Now these buildings are in various stages of decay. To protect these monuments of historic and artistic interest, it is most important to know first about the factors which affect the service life of the stones. The degree of decay of stones depends mainly upon the physical and chemical characteristics of the stones used along with the surrounding environment. The various factors, responsible for the decay of stones can be classified into three groups, (i) biological, (ii) chemical and (iii) physical.

1.1.1 BIOLOGICAL FACTORS

Biodeterioration of material may be defined as an undesirable change in the properties of a material caused by vital activities of micro-organisms (Hueck, 1968). Lohumi (1978) called the deterioration, caused by microbial action, the 'eczema' of building which is called 'Sur' in a local and Indian hill dialect or 'lonia' in Hindi. Besides the physico-chemical and climatic factors biological factors also play an important role in the deterioration of stones.

Among the biological factors, presence of algae, fungi, lichens, mosses and bacteria on the surface of stone monuments are important decaying agents. Although, a bloom of the growth may show a welcome and pleasing mellowness to a new surface, excessive growth can cause severe discoloration and disfigurement and accelerate physical damage of the stone surface (BRE 43, 1978). These growths occur on stone buildings under the favourable conditions of moisture, food and light. Table 1.1 shows the general requirements of food, light and humidity for different micro-organisms found over the stone surface. Freshly exposed rocks devoid of organic matter will be contaminated first by phototrophic micro-organisms (algae, lichen, cyanobacteria) followed very soon by heterotrophic micro-organisms (bacteria, actinomycetes, fungi). Rocks containing diagenetic organic matter may be colonized simultaneously by autotrophic and heterotrophic micro organisms (Eckhardt, 1985). The type and density of the growth depends

Table - 1.1

General Requirements for the Growth of Micro-organisms

Sl. No.	Micro-organisms	Food	Light	Humidity	Appearance
1.	Algae	Mineral Salts	Necessary	Necessary	Visible-coloring in strips or green, red, brown layers. Green black patina.
2.	Lichen	Mineral Salts	Necessary	Necessary	Visible - Hard, massive, leathery crusts usually orange or grey.
3.	Bacteria, Actino-mycetes and Fungi.	Organic material	Unnecessary	Necessary	Invisible even if associated with algae.
4.	Moss	Mineral Salts	Necessary	Necessary	Visible-Soft green, smooth vegetative structure, cushions of green to brown on humus deposited surfaces.
5.	Infesting grass and plants	Mineral Salts	Necessary	Necessary	Visible.

Reference?

upon the nature of stone, the climatic conditions and the degree of pollution (Richardson, 1976).

Several studies have been carried out to analyse the presence of these micro-organisms on the stone surface, their identification, and role in the stone decay and to prevent the development of these microbial population over the stone surface. Pierre and Giselle (1964) analysed the presence of bacteria, actinomycetes, mushrooms and algae in sandstone of Khmer monuments of Combodia, causing alteration of the monument. Pochon (1967) found the presence of sulphur bacteria, nitrogen fixing bacteria and nitrifying bacteria in the weathered crust of stone monuments. The limestone frescos in cathedral Bantis Taries in Padul has been found to be infected by fungi (Gargani, 1968). On headstones in War Graves Commission centres and various ancient monuments, growth of lichen, algae, mosses and even higher plants are clearly identifiable as the main cause of disfigurement (BRE News 36, 1976). Sulphur and nitrogen bacteria, fungi and actinomycetes were analysed on marble and sandstone of Taj Mahal (Techneco, 1977). Krumbein and Lange (1978) analysed the presence of green and blue green algae, fungi, bacteria, diatoms and lichens from the inside wall of a church in northwest Germany. In India, Sharma (1978) found abundant growth of moss, lichen, weeds and grasses in M.P. temples. The presence of cryptogamic growth was found on Dwarkadhish Temple, Sun Temple, Ellora and Jogeshwari caves by Lal (1978). Lenova et. al. (1980) analysed the presence of autotrophic and heterotrophic bacteria, algae, lichens and moss on plaster surface of the monument. Samidi (1981) found the presence of bryophytes, pteridophytes, lichens, algae, pustules, bacteria, fungi and actinomycetes on Borobudur Temple, one of the greatest Budhist monuments in Indonesia. Along the pores, cracks and fissures in the stone surfaces,these microorganisms may invade deeper into the stone structure.

The abundance of these micro-organisms may vary depending upon the nature of stone, depth and height of weathering zone and the climatic conditions favourable for the growth. Sulphur-bacteria have been found in very high number, as great as 10^4 per gm. of stone, the greatest number were found in the powdery zone but they were present at greater depths sometimes as much as 10 cm behind the scaling surfaces (Pochon, 1967). In one of the Greek Marble structures in St. Marks Church 1 to 10 million cells of sulphur bacteria were counted (Paleni and Curri, 1970). Barcellona et. al. (1976) examined the total number of autotrophic bacteria, algae, fungi and actinomycetes present in two Etruscan tombs. Eckhardt (1978) and Curri (1978) counted total number of heterotrophic bacteria, fungi and yeast from stone and dust material.

Some workers have isolated and identified these microorganisms. Eckhardt (1978) isolated 75 bacterial strains, 10 yeast species and 20 species of filamentous fungi in pure culture from the weathered crust of sandstone monument. Wagner and Schwartz (1967) isolated 41 strains of bacteria in the samples taken from the surface of rocks and developed on granite, orthoclase and felspar minerals. Udov et. al(1974) and Lebedeva et. al.(1977) identified various species of bacteria from the weathering crust of the rock.

Several workers have studied the role of micro-organisms in rock and stone degradation (Paine et. al. 1933, Krasilnikov 1949, Glazovskaya 1950, Omelyansky 1953, Webley 1963, Wagner and Schwartz 1965, Hueck-Vander Plas 1968, Friedman 1978, Eckhardt 1978, Krumbein and Lange 1978 and Karavaiko 1978) and have shown that in spite of the appearance factor, these micro-organisms corrode stones with the production of organic acids such as oxalic, citric, gluconic, glucuronic, due to their metabolic reactions and also through leaching and migration of certain constituents. The important characters of these micro-organisms and their degrading effects are described below :

1.1.1.1 Algae

Algae develop frequently on the stone surface under suitable conditions of dampness, warmth and light. They develop extremely rapidly within an hour or two of rainfall, usually becoming apparent as a bright green, but occasionally dark green, brown or pink coloration. During dry weather the algae die but spores will remain which permit growth to develop rapidly as soon as wet weather returns. Algal growth may occur on all types of buildings, surfaces in relatively unpolluted atmosphere (Richardson, 1976) and even in industrially polluted atmosphere (Dukes, 1972).

Green algae and blue-green algae (Cyanophyceae) are most widely found on the stone surfaces. Among Cyanophyceae, Coccales, Chrococus, Gloeocapsa, Microcystis, Lyngbya (Techneco, 1977), Scytonema, Oscillatoria, Nostoc (Samidi 1981), including Aphanocapsa, Aphanothese, Calothrix, Stigonema, Trentepohlia and Phragmonema (Grossin, et. al. 1978) have been identified from the surface of stone monuments. Cyanophyceae algae may prepare ground for heterotrophs to fluorish (Capelletti, 1967).

Among algae Coccoals can cause disintegration and perforation on the stone. Other forms like Gloeocapsa and Lyngbya are able to fix atmospheric nitrogen to produce nitrogen compounds, which are used by nitrobacteria thus causing further corrosion attack (Techneco, 1977).

1.1.1.2 Fungi

Deposits of dead algae and organic matter permit the development of fungi. Fungi are the main organisms in the penetration of rock particles and paint covers (Krumbein and Lange, 1978). Cladosporium, Phoma, Alternaria and Aureobasidium are some of the fungi reported on the stone surface (Richardson, 1980). Fungal filament may penetrate into the rock up to the depth of 3 to 6 mm (Krumbein and Lange, 1978).

Fungal hyphae penetrate into the stone not only by exploring cracks and fissures but also by generating organic acids (Richardson 1980). Eckhardt (1978) examined the presence of oxalic, citric, gluconic and glucuronic acid within the samples of sandstone monument as well as in the growth medium inoculated with isolated yeast and fungal species and suggested that these microbes excrete organic acids which contribute to weathering by acidifying the environment. (Henderson et. al. 1963, Schalscha et. al. 1967). These microbes are active in transforming feldspar and other aluminium-silicate to kaolin (Keller 1956, Friedman 1978). Eckhardt (1978) showed the fungal mycelia entrusted with minerals indicating the transformation of components of the monuments.

1.1.1.3 Slime Fungi

Slime fungi simply form a film of slime on the stone surface, which frequently incorporates trapped algae, giving it a green, or black appearance. Slime fungi occur in continuous dampness coupled with a suitable source of nutrient, for example, on the interior surfaces in cornish churches. These can also occur in some polluted conditions, where they can form a complete dense coating on stone surface (Richardson, 1980).

1.1.1.4 Mould

Mould, a kind of fungi, growth occurs on paint surfaces outdoors resembling a dirt-deposit (BRS Digest, 177, 1975). It also occurs on internal surfaces in presence of dampness.

1.1.1.5 Lichen

Algae lead to the growth of lichens by symbiotical relationship with fungi, normally ascomycetes. Lichens grow extremely slowly. Their activity increases in humid areas though they can tolerate extremes of temperature and survive for lengthy periods without moisture.

In some polluted atmosphere lichen growth is entirely suppressed, but pollution from fertiliser factories may result in accelerated lichen activity. Lecanora and Candelariella species of lichen are resistant to atmospheric pollution, developing particularly on limestone and other surfaces such as asbestos cement (Richardson, 1980). Oxides of nitrogen and sulphur are most likely to inhibit the growth (Dukes, 1972). However, some species tend to be concentrated in nitrogen rich conditions (Richardson, 1980). Calaplaca species are usually associated with limestone, whilst Tecidea and Rhizocarpa species are usually associated with sandstones (Richardson, 1980). Lichen have been found to sink their thallus to a depth of 10 mm in rock.

Lichen causes chemical deterioration of substrate by means of the end products of metabolism and mechanical disintegration through penetration of fungal hyphae (Salvadori and Zitelli, 1981). The secreted oxalic acid dissolves the carbonaceous stones such as marble, limestone and calcareous sandstone and redeposit as calcium oxalate in the thallus of lichen or beneath the thallus with the stone. The accumulation of oxalate increases with the age of the organisms, and is greater in the calcicolous lichen compared to the other species (Syers, et. al. 1967). The past presence of lichen growth can be detected on stone by examining the surface and detecting the dense calcium-oxalate deposits. A consistent accumulation (50%) of Ca-oxalate has been found in both mono and dihydrate forms associated with a living lichen thallus growing on marble monument (Salvadori and Zitelli, 1981). Besides the carbonaceous stone, these acids may also attack silica and cause etching damage on granite (Richardson, 1980).

1.1.1.6 Moss

The growth of mosses on stone or in joints usually indicate abnormally wet conditions. The development of moss is favoured over alkaline surfaces, such as cement concrete or lime mortars and it has been noted to take place on stone surfaces located near cement area (Torraca, 1981). Mosses develop only on the deposition of humus and cannot occur on fresh stone surface. The accumulation of deposits further permits to develop grasses, higher plants and eventually trees. Mosses can exert a definite disruptive action on the surface and upto a depth of a cm. or more.

1.1.2 CHEMICAL FACTORS

The modern urban industrial atmosphere is considered a prime cause for the chemical deterioration of stone monuments. The acceleration in the decay of stone used in monuments during the last few decades has been attributed to the sharp increase of air pollutants. The atmospheric pollutants relevant to stone decay are, sulphur oxides, carbon dioxide, nitrogen oxides and also ammonia, hydrogen fluoride, hydrogen chloride, fluorine and chlorine gases.

1.1.2.1 Sulphur Oxides

Pollution with sulphur compound is a major cause of the decay of building stones, which are commonly derived from the combustion of the organic and inorganic compounds of sulphur present in coal, coke and oil. (BRS Digest 1950). The two oxides - sulphur dioxide and sulphurous oxide - effect the calcareous material of the stones by forming the acids in the presence of atmospheric moisture or rain or moisture present on the surface of the stones. The chemical reactions involved are described below :

$$SO_2 \xrightarrow{+ 1/2\ O_2} SO_3 \xrightarrow{+ H_2O} H_2SO_4$$

$$CaCO_3 + H_2SO_4 + H_2O \xrightarrow{CO_2\uparrow} CaSO_4.2H_2O$$

$$CaCO_3 + SO_2 + 2H_2O \xrightarrow{CO_2\uparrow} CaSO_3.2H_2O \xrightarrow{+ O_2} CaSO_4.2H_2O$$

Since the gypsum formed is more soluble than calcite so the portion of buildings exposed to rain is usually washed out leading to a fresh surface of calcite for further attack. This results in the gradual dissociation of the stone. However, in the sheltered areas where the stone is protected from the direct impact of rain, a hard crust of gypsum is formed which leads to blistering and scaling of the surface.

Sulphuric acid also results into the rusting and disruption of iron bars used for joining of stone slabs due to the formation of hydrous iron oxide as shown below (Gauri and Holdren, 1981).

$$4\ Fe + 4H_2SO_4 + 2O_2 \longrightarrow 4FeSO_4 + 4H_2O$$

$$4\ FeSO_4 + O_2 + 6H_2O \longrightarrow \underset{\text{(Hydrous Iron oxide)}}{4FeO.OH} + 4H_2SO_4$$

1.1.2.2 Carbon dioxide (CO_2)

Atmospheric CO_2 forms the weak carbonic acid by the dissolution in rain water, which converts the insoluble calcareous ($CaCO_3$ and $MgCO_3$) matter of different types of stones into soluble bicarbonates causing the surface leaching in humid conditions.

1.1.2.3 Oxides of Nitrogen

Nitrous Oxide (N_2O), nitric oxide (NO) and nitrogen-di-oxide (NO_2) are present in the atmosphere. N_2O and NO may also oxidise to NO_2. NO_2 changes to nitric acid and effect the carbonate stones as follows (Amoroso and Fassina, 1983):

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4\ HNO_3$$

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

The nitrogen oxides also play catalytic role in the oxidation of SO_2, thus accelerating the decay of stones.

1.1.2.4 Halogen Compounds

Among the halogen compounds chlorine, hydrogen chloride, fluorine and hydrogen fluoride are present in the industrial atmosphere.

Hydrogen fluoride acts as a gaseous pollutant, reacting in the air and on calcareous stones to form Ca-fluoride, a stable and insoluble layer (Amorosa and Fassina, 1983, Vale and Martin, 1986) and on siliceous stones to form silicon tetra fluoride (Cortes and Martin, 1982, Vale and Martin, 1986)

$$2HF + CaO \longrightarrow CaF_2 + H_2O$$

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

Venetian marble is supposed to decay due to the presence of hydrogen chloride in venetian atmosphere (Lazzarini and Begolli, 1976)

$$CaCO_3 + 2HCl \xrightarrow{H_2O} CaCl_2.6H_2O + H_2CO_3$$

1.1.2.5 Ammonia

It is an alkaline gas derived from the volatization from animal excrements, fertilizers, soil and combustion process. An indirect effect of NH_3 on the deterioration of the stone, is its role in the aqueous oxiation of SO_2 which may further lead to the deterioration of calcareous minerals present in the stones.

1.1.3 PHYSICAL FACTORS

The physical factors mainly responsible for the decay of stones include salt crystallisation, temperature, wind, rain and frost. A brief description of these factors is presented below :

1.1.3.1 Salt Crystallisation

Salt crystallisation is considered to be a major cause of deterioration. It is caused mainly due to the reaction between atmospheric sulphur di-oxide and calcareous matter of the stone. The stone may attain an excess of soluble salts before quarrying or it may get contaminated by (i) ground water having salts from the soil, (ii) sea water that take water striking the coastal stone formations or salt carried at considerable distances by strong winds, (iii) due to chemical materials used in cleaning the stones and (iv) the mortar used in the construction of the building.

The movement of salts occurs along the surfaces as well as within the stone pore spaces. As a result soluble salts concentrate between the dry and wet zone of the stone surface. In dry conditions, vaporisation of water occurs resulting into further crystallisation and increase solid volume beneath the stone surface, the forces of excess solid volume within the pores can damage the stone in the form of spalling or exfoliation. In usual surface exposures salts are carried through the stone deposited at the outer surface as 'efflorescence'. The mechanism and disruptive effect of salt crystallisation was studied by many workers (Correns 1949, Chatterji and Jaffery 1963, Winkler and Wilhelm 1970, Winkler and Singer 1972, Binda and Baronio, 1987).

1.1.3.2 Frost

The stones which are exposed to freezing temperature by wet conditions may undergo frost damage. Water goes into the pores of the stone and attains its minimum bulk at 4°C. Between 4°C to 0°C it expands as it cools. Water changes to ice with a normal 10 percent expansion in the volume. The frost-resistance of a stone is often assessed from its saturation coefficient(=Water Absorption/Porosity), with stones having saturation coefficient less than 0.8 generally supposed to immune to frost damage. The form of frost damage includes deep cracking, surface scaling and exfoliation. Frost damage is an important factor of decay in the northern part of the United States.

1.1.3.3 Contour Scaling

Contour scaling is attributed to the repeated wetting and drying of the stone by rain and is called 'moisture rhythm'. Rainfall penetrates to more or less constant depth, where it dissolves a small fraction of the constituents of the stone. In the drying condition, the soluble matter is deposited at or near the surfaces. Repeated wetting and drying tends to consolidate the outer zone at the expense of cementitious matter in the underlying zone and results into the spalling of the surface. This spalling tends to occur to a consistent depth (BRS Digest 1950).

1.1.3.4 Thermal Stresses

During the day, sun warms the exposed stone surface more than the inside mass, at night radiation reverses the conditions. So an almost constant cycle of differential thermal stress is set up between the surface and the mass. In extreme conditions, when differential thermal stresses are greater, the stone particles are dislodged and microcracks are formed which widen with the stresses until the stone eventually spalls or cracks, e.g. thermal stress results in internal cleavage of calcite crystals in marble and also detachment of calcite crystals from one another. This effect is obviously higher in the regions where there is a considerable day-night temperature variations (Dukes, 1972).

1.1.3.5 Wind

Wind may cause deterioration of exposed stone surfaces from mechanical action exerted by particles present in the wind and from surface deposits of minerals and organic substances brought by the wind. Deposits of organic material may favour the growth of micro-organisms leading to further deterioration. Wind may also help evaporation of surface humidity resulting from environmental temperature and dampness and contribute to more or less rapid drying of the surface. In coastal areas, the eroding action of wind has considerable effect. (Frendiani et. al. I, 1978).

1.2 PRESERVATION OF STONES

Stone conservation processes have been classified as cleaning, consolidation and protection processes (Torraca 1976).

The cleaning of monuments of stone is not only necessary for a aesthetic reasons but it is required to ensure better preservation of materials. The cleaning process should be chosen, carefully on the basis of the characteristics of the stone, its state of decay and type of dirt deposited on its surface so that minimum quantity of stone is removed during cleaning. Cleaning methods commonly used are given below :

i. Water based methods : Water sprinkling, water spray, steam.

ii. Mechanical methods : Wet grit blasting, dry-grit blasting, microblasting.

iii. Chemical methods : Acid and alkaline solutions

iv. Absorbing clay packs and jelly pastes

v. Heat based methods : Pulse LASER

The aim of preservation and consolidation of stone work is to impart strength to weak and decomposed rocks and protecting them from atmospheric agencies. Heaton (1921) had defined the characteristics of a perfect stone preservative, which are given below :

(i) The stone preservative must penetrate easily and deeply into the stone, and remain there on drying.

(ii) It must not concentrate on the surface so as to form a hard crust, but must, at the same time, harden the surface sufficiently to resist erosion.

(iii) It must prevent penetration of moisture, and, at the same time, allow moisture to escape.

(iv) It must not discolour or in any way alter the natural appearance of the stone.

(v) It must expand and contract uniformly with the stone so as not to cause flaking.

(vi) It must be non-corrosive and harmless in use.

(vii) It must be economical in material and labore of application.

(viii) It should retain its preservative effect indefinitely.

Various workers have used different preservatives for the consolidation of weathered stones. The materials such as oil (Denekas, 1959), Wax (Hempel, 1968) and paints (Campoli, 1971) were tried as preservatives for surface protection of stone work. But, all these materials have since been avoided as they destroy the natural appearance of the stone. Further, they also resulted in the scaling off of the dense water proofing skin while the rest of the stone was left in a worse state of weathering than before. (Handbook, 1967).

Based on the type of preservative used, the preservation method may be divided into two types, (i) inorganic method and (ii) organic method

(i) Inorganic Method

This method has been used to modify the constituents of stone itself. The process is based on the precipitation of some inorganic materials such as Ca-silicate, $BaCO_3$ and silica, formed by the chemical reaction of treated solution and stone constituents. The product is insoluble in nature and is capable of binding together separated crystals of deteriorated stone.

Hemingway (1910) tried to precipitate calcium silicate and calcium chloride. Lewin (1967) used barium hydroxide and urea for limestone structures which form less soluble barium carbon[ate] or barium sulphate with calcium carbonate or calcium sulphate. This method has been successfully applied for the treatment of limestone and marble buildings in Britain. The process has been further developed by Lewin (1970) and Lewin and Baer (1974) by the precipitation of barium carbonate from barium chloride and barium hydroxide solutions introduced in the pore space of the stone. However, only limited penetration of the hydroxide was achieved during surface application and in practice this treatment was also proved to be a failure. Recently, Rao (1980) found this treatment inapplicable for granite statues.

Silicone esters such as ethyl silicate, was used for introducing silica into stone as a consolidant. On hydrolysis, ester breaks down to silica and alcohol (King (1931), Shore (1957), Liberti (1959), and Lassakaya (1961, 1962), Wihr and Steenkan (1971), Somto (1985)). Solutions of Magnesium and zinc flurosilicate were used by Schaffer (1955), Sampaolesi (1966) and Knappwost (1986). These treatments in some cases have been found to promote salt accumulation beneath the treated surface layer causing spalling of the treated layers.

However, in general, inorganic consolidants have good resistance to ageing by light and oxygen but show low resistance to mechanical shock (Torraca, 1981).

(ii) Organic Method

The second method of preservation is the application of organic compounds which aims to introduce an organic adhesive between the dislodged grains of the stone. Organic consolidants improve the mechanical properties of stones, however, the resins are themselves slowly deteriorated under the action of oxygen and light and acid (Torroca, 1981; Tucci, et al. 1985). This method has been commonly used in India as well as abroad and is carried out by the introduction of monomers and polymers into stones. Monomer is polymerised in-situ by means of a catalyst (Munnikendam,1971-a) or gamma-radiation (Nadaillac,1972). The polymer filled in pores of the stone develops consolidation, water repellency and surface protection. The polymers generally used for this purpose are silicone resin, epoxy resin, acrylic resin, polyester resin, fluorinated compounds and silane.

Lenz (1968) applied a mixture of unsaturated polyesters and styrene to sandstone statues, bricks and wooden objects. Polyester resins have also been used for glazing stone, concrete, metal, and glass surfaces (Rasul, 1966). Use of polyurethane resin increased the resistance to moisture and temperature changes (Harada, 1975). However, polyesters show a relatively high surface-weathering rate when directly exposed to the environment (Torraca, 1976).

Esso Standard Societe (1964) treated the limestone, with 20-35% solution of thermoplastic resins resulted into improved compressive strength, plaster adhesion. Munnikendam (1971-b) tried methyl-methacrylate (MMA) with peroxide and amine at room temperature. He (1972) established that this process could not be employed with larger structures. The use of cross-linking agents such as trimethylol propane-tri-methyl-acrylate has been studied by Fowler et. al (1973) for achieving adequate polymerisation rates at relatively low temperature. De Long (1977) used a mixture of acrylic acid and alkyl methacrylate and found suitable against salt water action and air pollutants. deWitte et. al (1978) used a mix of MMA and ethyl acrylate and found that polymerisation temperature has a major influence on the polymerisation behaviour. Pearson (1982) applied MMA monomer on buildings and monuments by insitu polymerisation at ambient temperature. These acrylic resins have been found to have good water repellent properties (Charola et. al. 1985).

Among the epoxies two basic types (controlled by their viscosities) have been used in stone preservation. Domaslowski (1969) tried more viscous epoxies of type Bis phenol-A diluted with a solvent. Gauri (1970) used a combination of such epoxies, solvents and epoxy diluents (low viscosity aliphatic epoxies). Munnikendam (1973) used the epoxy diluents only as stone consolidants. Gauri (1974) has shown that the aliphatic epoxies absorb SO_2 and therefore, increased the chemical reactivity of treated stone in laboratory test. He (1978) also reported the relative merits of specimens treated with flurocarbon-acrylics, epoxies and silicones and concluded the combined use of epoxies and flurocarbon-acrylics for consolidation and surface protection. Marinelli (1976) and Krieg (1978) also discussed the use of epoxy resins. However, epoxy resins have a tendency to discolorise and oxidise when exposed to light (Torraca, 1976).

Silicone Resins have been very commonly used in consolidation of stone monuments. Richardson (1961) sprayed 5% solution of methyl and phenyl silicone resins and petroleum (as a solvent) on a damp external masonry wall to form a water proof surface. Sobolevskii et. al (1972) reported the use of organosilicone compound resulting into the considerable decrease in water absorption and increase in durability and resistance to frost and sea-water. Lehmann (1976) used dilute solution of silicone resin for the protection of stone against all factors such as atmospheric pollutant, rain, temperature, humidity and the biological agents. Gerad (1972) and Mamillan (1972) carried out research to evaluate the performance of commercial types of silicones, their results showed differences of behaviour among the products of different manufacture. Weber (1976) reported that silicone resin turned out to be the most successful consolidant. Impregnation will remain effective for at least 10 to 15 years and resist to UV radiation due to their 'SiO_2' structure. Penkala et. al (1978) also found silico-organic compound suitable for protection of monuments.

In modern conservation practice silanes have been accorded much attention. The silanes used are alkoxy or alkyl-alkoxy silane. Price (1975) reported the use of alkoxy silanes for several exposure trials at a number of sites representing different types of stone and exposure conditions. Hempel (1976) reported on their trial treatments with a silicone resin which is based on trimethoxy methylsilane and concluded the best present consolidant for deteriorated carbonate stones. Recently, Heiman (1981) gave information for successfully using the mixture of alkyl alkoxy silane, ethyl silicate and ethanol. Nishiura (1981) reported the merits of methyl triethoxy silane for porous siliceous materials. It chemically combines with siliceous materials. Sramek et. al (1981) studied the effect of ultra violet radiation and SO_2 on MMA, alkyl alkoxy silane, epoxide resin, polyester and found that the silane has the most stability. The order of stability was found as silane >> MMA >> epoxide >> polyester.

Nonfarmale (1976) and Bergonzoni (1981) applied a mixture of silicon and acrylic resin on sandstone buildings. Rossi (1976) studied the effectiveness of different preservative namely silicone resin, acrylic resin, epoxy, alkyl silicate, and silane alone and with mixture of each other in laboratory and also studied the depth of penetration and colour change by the treatment. Recently (1981), he tried the mixture of silicone acrylic resin, silicone ester and silane. A mixture of ethyl acrylate, styrene, phthalic anhydride, dioctyl maleate, glycol, varsol and naphthenate have been found effective for sandstone, marble and concrete having good resistance to efflorescence and fungi by Gaertner (1977).

1.3 PREVENTION OF MICROBIAL GROWTH

Several studies have been carried out to use the suitable biocide to inhibit the growth of such microbial character. A number of biocide have been tried from time to time, such as household bleach, Na-O-phenyl phenate and pentachlorophenate, formaline (40%), Zn-Mg fluorosilicate, nuodex.87(1-5%), copper carbonate with ammonia solution, organotin quaternary ammonium compound and borate polybor (BRS Digest, 1972) among which quaternary ammonium compound (1%) alone and with tri-butyl tin oxide have been found most effective (Richardson 1976, BRS Digest 177, 1975, Samidi, 1981). Zissis (1957) found successful application of penta-chlorophenol to kill the lichen growth on marble monuments. However, Richardson (1976, 1980) found Na-pentachlorophenate and Na-methyl siliconate with pentachlorophenate or phenyl phenate unsuitable as their use resulted into the formation of deposit and staining the stone surface. The application of phenolic solutions and mercurials are considered risky to operatives. Dupuy et. al (1976) described the use of fluorosilicates, Cu compounds and complexes, antibiotics, hyamines and ammonia salts to prevent the growth of blue green algae on stone monuments.

Frendiani et. al : 2 (1978) carried out various treatments and the results showed that hydrogen peroxide is not as effective at low concentrations, 60 volumes, as at 120 volumes, but this may result red or black spots on the surface of the stone and formaldehyde (40%) may form a deposit on the surface.

Alessandrini et. al (1978) used acrylic silicone resin and epoxy aliphatic resin which retarded the growth of algae to a considerable extent. Curri (1978) studied the growth inhibiting activity of some biocides and concluded that Isothiazoline chloride had the maximum of biocidal activity besides at very low concentration. Benzalkonium chloride was also found effective in inhibiting the algae growth (Grant and Bravery, 1985). Vander et. al (1980) used successfully a mobile UV unit (MUVU) to control the growth of algae and cyanobacteria occuring on the plaster covered interior walls of the Church in Germany.

In India, so far no concerted efforts have been made to study the biological growth and their prevention. However, Lal (1978) and Sharma (1978) studied the use of ammonia water for the elimination of the growth and dilute solution of Zn-silico-fluoride to check the redevelopment of these growth effectively. Treatment with zinc silico fluoride followed by thin solution of polyvinyl acetate or polymethyl methacrylate was found to be more effective.

The above literature survey clearly indicates that although a good deal of studies have been carried out on the causes of deterioration of stones and stone monuments, no correlation on the properties which indicate or predict deterioration, has been established. There is a clear gap of scientific information on the prediction of durability of a particular stone in a specific environment or durability cycles of wetting, heating and cooling, particularly in hot and humid tropical climatic conditions prevailing in India. It is, therefore, considered of timely importance to investigate the mechanism of decay of stones used in various monuments and buildings and find out suitable preservatives to check the physical, chemical and biological factors responsible for the decay of stones.

The present study embodies the results of the major causes of decay of building stones (freshly obtained from quarries and also the same types used in historical buildings and monuments of India). The study also includes the effectiveness of different preservatives namely barium hydroxide, styrene, polymethyl methacrylate (PMMA) and for the same building stones. The stone samples collected for this study were examined for their mineralogical, physico-chemical and durability behaviour before and after the treatments with above preservatives at various intervals of durability tests under varying environmental conditions. An attempt has also been made to establish a relationship of the decaying behaviour with the physical properties of the stones used in the monuments. These relationships established for the stones examined can be considered as standard curves for assessing and predicting the life of similar stone used in the monuments at different places. The present investigation includes the identification and characterisation of microbial growth commonly found over the stones and their role in various modes of decay and deterioration of the stones. The effect of above preservatives to retard the growth of microbial population over the stone surfaces has also been studied.

CHAPTER II

EXPERIMENTAL PROCEDURES

CHAPTER II

EXPERIMENTAL PROCEDURES

The present chapter describes the experimental procedures followed for carrying out biological, physico-chemical and preservation studies given in text books and standard specifications.

2.1 BIOLOGICAL STUDIES

2.1.1 Materials

In the biological study the microbial growth occuring on the stone monuments were identified. For this study the samples of microbial growth were collected from famous historical monuments of Delhi namely Red Fort, Jama Masjid, Purana Qila, Kotla Firoj Shah and Qutb Monuments. These monuments are mainly constructed of red and white spotted sandstones, white and black marble, rubble and also of some coloured stones. A brief history of these monuments is given in Table 2.1.

2.1.2 Collection of Microbial Samples from Stone Surfaces

The samples were collected from above mentioned Delhi monuments during rainy season in the month of September - years normally after three days heavy rains. The multiple samples were collected from each site. The material was scrabbed from stone surfaces with the help of sterile spatula and brush, stored in plastic tubes and fixed in 4 percent formaline solution on the spot.

Table 2.1

Historical Details of the Monuments (Reference

Sl. No.	Name of Monument	Year of construction	Type of stone used	Built by
1.	Red Fort	1639-1648	Red sandstone and marble	Shah Jahan
2.	Jama Masjid	1644-1650	Red sandstone and marble	Shah Jahan
3.	Kotla Firoj Shah	1351-1388	Rubble	Firoz Shah Tughluq
4.	Purana Qila	1541-1544	Red sandstone and marble	Sher Shah Suri
5.	Qutb Minar	1198-1236	Red sandstone and marble	Started by Qutbu'd-Din Aibak and completed by Shamsu'd Din Iltutmish.

2.1.3 Preparation of Slides

The fixed material was taken out from the plastic tube by forcep and put on the slide. It was teased with the help of forcep and needle. The material was mounted in glycerin diluted with 4 percent formaline solution. A coverslip was put over the material in the centre of slide carefully that no air bubble remains in between the slide and coverslip. After ascertaining that the material was teased fully and uniformly, it was sealed with DPX Mountant. Multiple slides were prepared of each sample.

2.1.4 Study of the Slides

The slides were studied under 10 x10, 40 x 10 and 100 x 10 magnifications. For study under 100 x 10 magnification (oil immersion lense), a drop of paraffin oil was put on the coverslip after the slide was fixed on the microscope. The measurements of the cell were taken under oil immersion lense with ocular micrometer. The value of one division of ocular micrometer was estimated to 1.8μ.

Using the data of length, breadth, with and without the sheath and other important characters of the cell such as colour and shape, the cells were identified by the characters mentioned by Desikachary (1959).

Camera lucida of the species have drawn under oil immersion lense (100 x 15 magnification). The microphotographs of the slides were taken with the help of microscope, 'Reichart-Jung Neover-2', using 'Praktica B' camera.

2.2 PHYSICO-CHEMICAL STUDIES

2.2.1 Materials

For carrying out physico-chemical, durability and weathering tests, the chemicals like, Na_2SO_4, $CaSO_4.2H_2O$, $MgSO_4$, $MgCl_2$, $BaCl_2$, $Ba(OH)_2$, H_2SO_4, HCl, Urea, Acetone etc. of AR grade were used. The preservaties styrene and polymethylmethacrylate of AR grade procured from M/S Lab Instruments and Chemicals, Delhi and silicone resin 5081 from M/S Laboratory Chemicals Co., Bombay was used.

2.2.2 Collection of Stone Samples

The samples of stones selected for this study were collected from the monuments as well as from the quarries. The samples of fresh red and white spotted sandstone were collected from quarry, Hindon (Rajasthan) and pure white Makrana marble from quarry, Makrana (Rajasthan). The basalt samples were collected from Elephanta Cave, Bombay. Efforts were made to collect the basalt samples already got removed from the sculptures as well as from the side walls. The scoria samples were collected from the Rammappa Temple, where it has been used on the top.

2.2.3 Physical Tests

About two hundred cubes ($2.5 \times 2.5 \times 2.5\ cm^3$) of each type of stone were cut to the sizes required as per I.S. specifications for carrying out physical, durability and weathering studies. Samples were thoroughly washed under tap water followed by immersion in luke warm water (40-50°C) to remove the dust. The samples were then dried in an oven at 100-110°C for 24 hours. Unless stated otherwise the tests were carried out as per IS specifications. A brief description of the procedures is given below:

2.2.3.1 Water Absorption and Porosity

Water absorption and porosity characteristics of stone samples were determined as per IS:1124 (1974) described below:

The stone pieces were immersed in a 1000 ml beaker containing distilled water and the entrapped air from the stone pieces got removed by gentle agitation using a rapid clockwise and anti-clockwise rotation manually. After 24 hours, the pieces were removed and the surface moisture was completely wiped off with the help of dry cloth. The samples were then weighed on a single pan balance with a least count of 0.1 mg. The volume of the sample was determined by the displacement of water in graduated cylinder. In order to get the dry weight, the samples were first dried in oven at temperature 100-110°C for 24 hours and then weighed.

Estimation of Water Absorption

Water absorption values were calculated using the following formula:

$$\text{Water Absorption } (\%) = \frac{B - A}{A} \times 100$$

where,

A = weight of oven dried stone piece in gm

and B = weight of water saturated stone piece in gm

Estimation of Porosity

The porosity values of the samples were calculated from the following formula :

$$\text{Porosity } (\%) = \frac{B - A}{V} \times 100$$

where,

A = weight of oven dried stone piece in gm

B = weight of water saturated stone piece in gm

and V = volume of stone piece in cc

2.2.3.2 Apparent and True Specific Gravity

Apparent specific gravity was determined by standard procedure (IS:1124) whereas the true specific gravity was obtained using Le-Chatelier method which is described below:

The stone sample was ground and passed through IS sieve of 150 micron. The fine material was first dried at temperature 100-110^{o}C for 24 hours and then cooled in a dessicater. This material (50 gm) was slowly introduced in a dry Le-Chatelier flask filled with kerosene oil upto its zero mark. Entrapped air was removed gently by rolling and tapping the flask. The flask was then kept at room temperature for 24 hours. The increase in the level of kerosene oil in the flask was noted and true specific gravity was estimated :

$$\text{True Specific Gravity} = \frac{M}{B - A}$$

where

M = 50 gm of dried sample

A = Initial reading of kerosene oil in the flask before adding the stone powder.

B = Final reading of kerosene oil in the flask after 24 hours.

2.2.3.3 Bulk and Real Density

Density measurements were made according to standard procedure described in Unesco Rilem (No. 1.2, 1978). Oven dried and weighed samples were saturated in distilled water in a vacuum dessicater to displace the entrapped air completely from the pores of the samples. The samples were then left in water for 24 hours and then weighed separately in water. The wet weight of the samples were determined after wiping off surface moisture.

Estimation of Bulk Density

The following formula was used for calculating the Bulk Density :

$$\text{Bulk Density} = \frac{M_1}{M_3 - M_2}$$

where

M_1 = Mass of oven dried sample

M_2 = Mass of water saturated sample, under vacuum, in water.

M_3 = Mass of water saturated sample, under vacuum, in air.

Estimation of Real Density

Real density was calculated by using following formula :

$$\text{Real Density} = \frac{M_1}{M_1 - M_2}$$

where

M_1 = Mass of dried sample

M_2 = Mass of water saturated sample, under vacuum, in water

2.2.3.4 Compressive Strength

Compressive strength of stone was determined by the standard procedure as described in IS:1121 (1974).

The load was applied with a testing machine on the stone surface without shock and increased continuously at a rate of approximately 140 kg/cm^2/min. until the resistance of the test piece was exhausted and the cracks developed in the stone structure. The maximum load applied to the test piece was noted and the appearance of stone was recorded. The compressive strength of the stone was calculated as follows :

$$\text{Compressive Strength} = \frac{\text{The maximum load supported by the stone piece before failure}}{\text{Area of the bearing face of the pieces}}$$

2.2.4 Chemical Analysis

Samples were ground and passed through 150 µ sieve. The sieved samples were subjected to determine the silica, iron, aluminium, calcium and magnesium oxides content as per standard methods (Vogel, 1967).

2.2.5 Petrography

The petrographic studies were carried out under 'Panphot Leitz' microscope. Thin sections of fresh and disintegrated stone pieces were prepared as per standard method (Moorehouse, 1959). All the sections of the stones were examined in plane polarised light as well as between the crossed nicols. Structural, textural and grain size variations in the samples were determined.

2.2.6 Treatment with Preservatives

The preservatives 25 and 50 percent silicone resin (SR) (V/V), and 5, 10 and 15 percent polymethylmethacrylate, (PMMA) (W/V) in acetone, styrene solution containing 3 percent benzoyl peroxide (W/V), and 8 percent barium hydroxide ($Ba(OH)_2$) (W/V) containing 4 percent urea (W/V) were used. The application methods of these preservatives are described below :

The stone samples were immersed in preservatives solution of indicated strength in a glass truff, which was put in vacuum dessicater connected to a vacuum pump. The vacuum was applied until all the air bubbles were removed. The process was repeated after changing the sides of stone pieces to ensure complete removal of air and impregnation. The samples were allowed to remain immersed in solution under pressure overnight and then dried at 60^{o}C.

In the case of styrene, samples were wrapped and tied in Al-foil to minimise the evaporation during polymerisation of styrene and were kept at 70°C for overnight to complete the polymerisation in stone itself.

In $Ba(OH)_2$ treatment, marble samples were immersed in the solution for one weak continuously, during which sides of samples were changed regularly to obtain a uniform treatment.

Triplicate samples of each variety of stone were treated with each preservative by brushing also. At least three coats were applied on each sample to ensure complete surface coating. After four weeks of the treatment samples were subjected to different tests.

2.2.7 Weathering Test

Procedure IS:1125 (1974) is used to find out the resistance of stone towards corrosive ground water, wetting and drying, sulphate attack and temperature variations.

The oven dried untreated samples were weighed after cooling them to room temperature and immersed in distilled water. The samples were removed after 24 hours, wiped and weighed.

Each test piece was placed in a flat glass dish, 9 cm in diameter and 1.5 cm in depth; 2.0 gm of powdered gypsum and 25 ml of distilled water was added in each dish and the dishes with specimens were placed in an oven at 100-110°C temperature for at least 5 hours so that the water had evaporated and the powder became dry. The dishes were removed from the oven and cooled to room temperature. This completed the first cycle.

The samples were subjected to 100 cycles of the test in the same manner, except that only 25 ml of water was added for each of the subsequent cycle.

Duplicate samples were removed after every 10 cycles of the test and particles of gypsum were removed by brushing the surface followed by washing with distilled water to remove gypsum deposited on the surface and pores of stone pieces. After washing, the samples were dried, cooled and weighed before and after immersion in distilled water to get dry and wet weights respectively. Water absorption and porosity of each test sample were calculated as discussed earlier. The change in weight was calculated as follows :

$$\text{Change in weight } (\%) = \frac{M_I - M_F}{M_I} \times 100$$

where

M_I = Initial weight of oven dried sample

M_F = Weight of oven dried sample after test cycle.

Weathering Test was only carried out on untreated stones as the untreated samples themselves did not show any disintegraties upto 100 cycles of the tier.

2.2.8 Durability Test

The salt crystallisation test for assessing the durability of building stones has been used since 1828 (Brard). The crystallisation test was one of the test selected by

RILEM 25 PEM working group for inter laboratory validation (Price, 1978). It is an accelerated test to assess the resistance to decaying agents, especially the damage caused by salts on both untreated and treated stones. The test is also useful for showing the behaviour during decay of the contact zone between the impregnated surface layer and the mass of stone remained unreacted by the impregnation (Unesco Rilem V.1b, 1978). The destruction effect of Na_2SO_4 filling the pores is mainly due to increase in its volume by 4-folds during transition to $Na_2SO_4.10H_2O$, in the water solution at a temperature of 32.7^oC (Marschner, 1978).

By the immersion of stone samples in $Na_2SO_4.10H_2O$ solution, it penetrates the samples. On drying the samples anhydrous Na_2SO_4 crystallises within the pores of stones. After drying, samples were cooled to room temperature and reimmersed in the solution to allow further penetration of fresh $Na_2SO_4.10H_2O$ solution and already formed anhydrous Na_2SO_4 within the stone pores to get converted to decahydrated state. This repeated wetting and drying of samples cause repeated transformation from one state to another resulting in large change of volume of salt crystals within the pores of stone samples. As a result a sufficient pressure developes on the walls of the pores causing disintegration of stone samples in the form of cracks etc.

The durability test methods mentioned in IS:1126 (1974) and Unesco Rilem specification (V. Ia, 1978) have different parameters such as concentration of salt solution, immersion time, drying time and temperature.

In the present study the durability of untreated stones was studied under the following test conditions (Table 2.2).

Table 2.2

Different Durability test Conditions for Untreated Stones

Test Condition	Concentration of Na_2SO_4 sol. (%)	Immersion Time (hrs)	Drying Time (hrs)	Drying Temp. (^oC)
1	18	16	5	105 ± 5
2	18	5	16	105 ± 5
3	18	5	16	60

Test condition (1) is standard method as per IS:1126 (1974). Test condition (2) was carried out to study the effect of immersion and drying time and test condition (3) for studying the effect of drying temperature.

The durability behaviour of the samples treated with different preservatives was assessed as per test condition(3). The drying temperature of 60°C was chosen instead of a higher one in order to prevent the deterioration of organic resins, (Unesco Rilem V. Ib; Marschner, 1978).

The untreated stone samples were subjected to test cycles to the extent of disintegration and the treated samples were carried out upto the decay of stones or 100 cycles of test method.

For the evaluation of the progressive change in the physical and durability characteristics the stone samples were taken out during durability test. All such samples were thoroughly washed with distilled water to remove the salt deposited and then dried, cooled and weighed.

2.2.9 Sea-Water Test

To study the effect of sea water on the monuments situated in the coastal regions, test samples of different stones were subjected to durability test in simulated sea water, prepared with following compositions:

32 gm/litre NaCl, 10 gm/litre $MgCl_2$, 12 gm/litre $MgSO_4$ and 0.5 gm/litre $CaSO_4.2H_2O$.

In the test cycle stone samples were immersed in simulated sea water solution for 5 hours followed by drying at 105°C (in the case of untreated stones) and 60°C (in the case of treated stones) for 16 hours. Samples were subjected to 50 test cycles. After every 10 cycles, duplicate stone samples were removed and thoroughly washed with distilled water. Water absorption, porosity values and change in weight were calculated as per method described earlier.

2.2.10 Acid Test

Several types of natural building stones show rapid deterioration by atmospheric sulphur dioxide in an polluted atmosphere. To study the behaviour of sulphur dioxide polluted atmosphere on different stones their immersion in sulphuric acid solution of different concentrations has been considered as a tool in different standards. According to IS:4122 (1967) sulphuric acid of 1 percent (by weight) concentration has been used to study the surface softening of natural building stones by exposure to acidic atmosphere. In BS:3798 (1964) 11.9 percent sulphuric acid solution (by volume) has been mentioned for standstones, whereas 0.54 and 2.75 percent (by volume) have been recommended to slate; which may show the effect of slight to moderate and high atmospheric pollution respectively.

In view of above tests, in the present study, 0.5, 1.0, 2.0, 5.0 and 10.0 percent H_2SO_4 solutions (V/V) were used to know the behaviour of the stones in slight to highly acidic polluted atmospheric environments.

Stone samples of each variety were immersed in H_2SO_4 solutions of different concentrations as indicated above at room temperature. After 10 days, the samples were removed from the respective solution and thoroughly washed with water. The untreated stones were dried at 105°C while the treated samples at 60°C. The samples were cooled, weighed and the change in weight was measured.

CHAPTER III

BIODETERIORATION OF STONES

CHAPTER III

BIODETERIORATION OF STONES

3.1 INTRODUCTION

Biological factors, play an important role in the deterioration of stones. These factors are closely interrelated with physico-chemical factors which cause damage to stones (Curri, 1979; Richardson, 1980). Deterioration, where it appears to be purely physical or chemical, gets further accentuated by micro-organisms (Pochon, 1967). Many deterioration processes, which were known to be physico-chemical in nature have been established to be mediated by micro-organisms. The presence of micro-organisms, even in greater number on weathered material does not necessarily imply that these organisms have caused the observed damage. However, these populations may be involved in enhancing the decay processes (Eckhardt, 1978).

In the present study efforts have been made to identify the microbial growth occuring over stone monuments and to find suitable preservative to retard their growth over the surfaces of stones.

3.2 EXPERIMENTAL PROCEDURES

The microbial samples were collected from Red Fort, Jama Masjid, Purana Qila, Kotla Firoj Shah and Qutb monuments, situated in Delhi (Fig. 3.1). These monuments are mainly

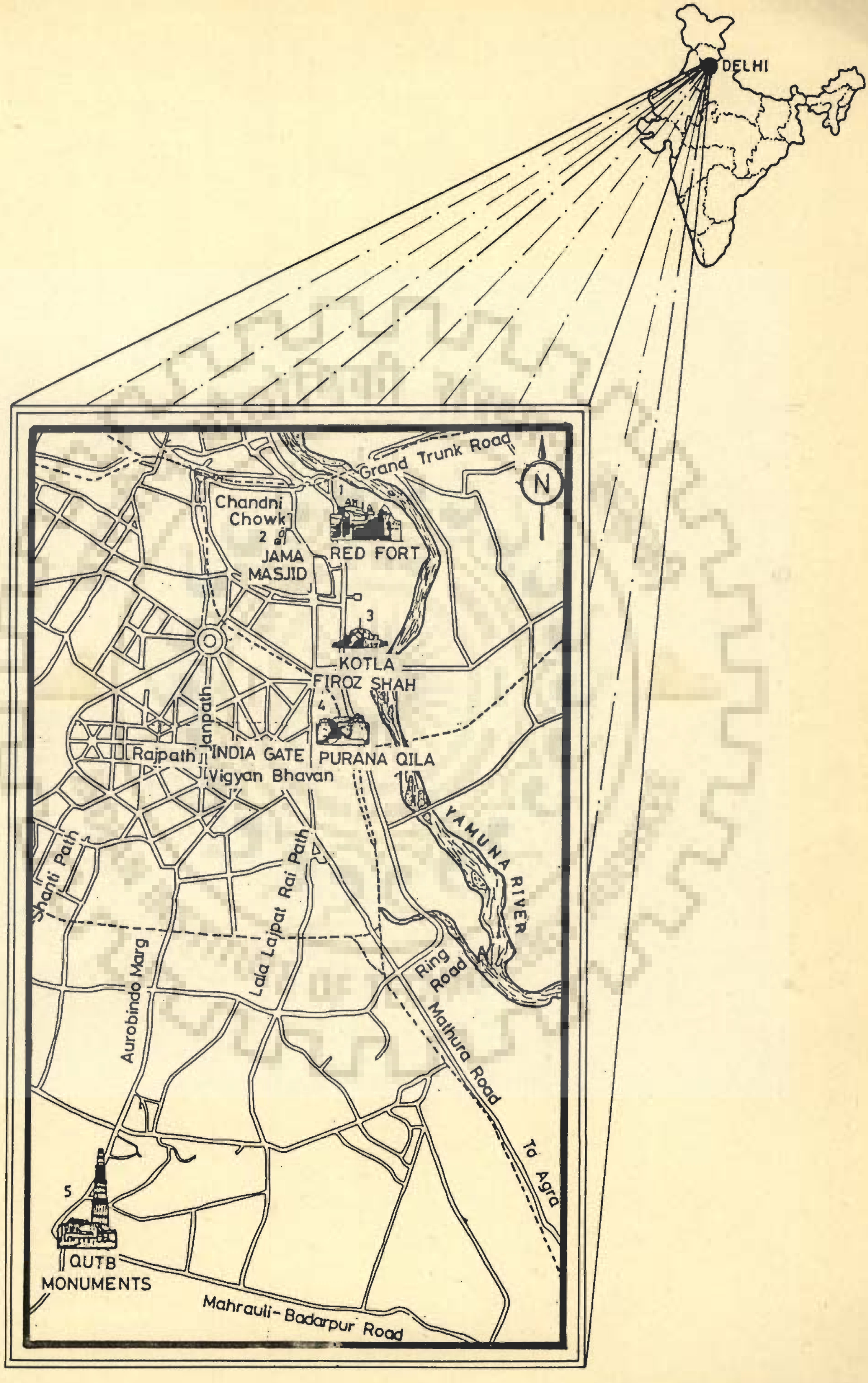


FIG.3·1. SITES OF COLLECTION OF MICROBIAL SAMPLES FROM MONUMENTS OF DELHI constructed of red and white spotted sandstone, white and black marble alongwith some coloured stones. The method of collections of microbial samples from the stones surfaces, preparation and study of slides were carried out as described in Chapter II.

Table 3.1 summarises the different points of collection of micro-organisms along with the nature of substrate and visual appearance of microbial growth. The samples of micro-organisms were commonly collected from different points such as outersurface, joints, carvings and cracks of the above mentioned monuments which was found to be fresh in the form of light or dark green layer though at some places it was in the form of a dried blackish layer. In Jama-masjid the growth was completely dried in for the form of black spots. Generally, the microbial growth was found to be present on stone itself, however, at some sites (site no. 3 and 4) the growth was appeared to grow first on mortar material and then it spread on the stone surface.

The effect of preservatives namely barium hydroxide solution, polymethylmethacrylate (PMMA) and silicone resin on the growth of mixed microbial samples (algae and moss) have been studied in petridishes having the following culture medium : (Ref.)

$Ca(NO_3)_2 \cdot 4H_2O$	1g
$MgSO_4 \cdot 7H_2O$	0.250g
KCl	0.250g
KH_2PO_4	0.250g
$FeCl_3$	0.1 ml (1%)
H_2O	1 l
pH	[illegible]

Table - 3.1

Collection of Micro-Organisms Found On Different Points of Stone Monuments

ample No.	Sites For the Collection	Substrate	Appearance of Microbial Growth
	RED FORT		
i)	Outside wall at the entrance	Red and White spotted sandstone	Dark green layer
ii)	Side wall of Shahi Hammam	Red sandstone	Greenish and Blackish layer
iii)	Deteriorated structure in the lawn near Shahi-Hammam	Red sandstone	Greenish and Blackish layer
iv)	Horizontal and Vertical joints in the wall of Rang Mahal (near the stair - cases)	Red sandstone	Greenish layer
v)	In the carvings of the wall in Diwan-I-Khas (near the staircases)	Marble	Greenish, slightly dried
vi)	Around the boundary of Central space in Moti-masjid	Marble	Dark green layer
	JAMA-MASJID		
vii)	In the carvings of the wall and pillar	Red sandstone and Marble	Black dried spots difficult to scrab
viii)	Around the boundaries of Central tank, filled with water	Marble	Dark green and brown red layer
ix)	In the mortar joints in the staircases of back entrance	Red sandstone	Dark green and Light green layer

Table-3.1 Contd.

KOTLA FIROJ SHAH			
(x)	Walls	On mortar material	Dark green layer
PURANA QILA			
(xi)	Walls of the museum and on the roof	On mortar material and quartzitic stone	Green layer and Dried blackish layer
QUTB MONUMENTS			
(xii)	Side wall of IInd entrance gate of Qutb Minar (The place of drinking water)	Quartzite	Green layer
(xiii)	Outer boundary of lawn in Qutb area	Quartzite	Green layer
(xiv)	In the joints of wall of Quwwatu'I Islam Masjid	Quartzite	Green layer

The microbial samples in culture medium were grown in petri-dishes with and without preservatives for 15 days at room temperature.

3.3 RESULTS AND DISCUSSION

3.3.1 Identification of micro-organisms found on the stone monuments

A study of slides of micro-organisms showed the presence of Cyanophyceae (blue-green) algae and moss in the collection. Although no fungus or lichen growth was found to be present in the samples, the spores of Alternaria, fungus, were present (plate 3.4c) in one sample from the monument Kotla Firoj Shah (site no. 3). Identification of Cyanophyceae algae was based on Desikachary (1959). Table 3.2 shows the microbes identified alongwith their points of collection. Table 3.3 describes the important characters and measurements of various species of Cyanophyceae algae identified. Altogether 17 species of 9 genera of 4 families of Cyanophyceae algae could be identified (Table 3.4). The four families are Chroococcaceae, Oscillatoriaceae, Nostocaceae and Scytonemataceae. The three genera of Chroococcaceae are Microcystis, Gloeocapsa and Aphanothese. The two genera of Oscillatoriaceae are Oscillatoria and Lyngbya. The two genera of Nostocaceae are Nostoc and Cylindrospermum and the two genra of Scytonemataceae are Scytonema and Tolypothrix. Altogether three species of Gloeocapsa, four of Oscillatoria, three of Lyngbya, two of Scytonema and one of each of others

Table 3.2

Algal and Moss Population Identified From Different Points of Collection From Monuments:

Sample No.	Sites for the collection	Microbes
	RED FORT	
(i)	Outside wall at the entrance	Aphanothese pallida, Oscillatoria pseudogeminata
(ii)	Side wall of Shahi Hammam	Funaria (green layer) Gloeocapsa livida, Lyngbya truncicola (blackish layer)
(iii)	Deteriorated structure in the lawn near Shahi-Hammam	Funaria (Green layer) Gloeocapsa kuetzingiana (blackish layer)
(iv)	Horizontal and Vertical joints in the wall of Rang Mahal (near the staircases)	Nostoc paludosum
(v)	In the carvings of the wall in Diwan-I-Khas (near the staircases)	Lyngbya truncicola, Tolypothrix byssoidea
(vi)	Around the boundary of Central space in Moti-masjid)	Lyngbya martensiana Var. Calcarea, Lyngbya allorgei, Oscillatoria pseudogeminata
	JAMA-MASJID	
(vii)	In the carvings of the wall and pillar	Dried, couldn't be identified
(viii)	Around the boundaries of Central tank, filled with water	Microcystis pulverea, Oscillatoria formosa, Oscillatoria schultzii.
(ix)	In the mortar joints in the staircases of back entrance	Oscillatoria pseudogeminata, Oscillatoria jasorvensis, Lyngbya truncicola, Cylindrospermum musicola.

generic names should be underlined

Table 3.2 Contd.

	KOTLA FIROJ SHAH	
x)	Walls	Scytonema hofmanni
	PURANA QILA	
xi)	Walls of the museum and on the roof	Funaria, Riccia (green layer) Dried Cyanophyceae algae (mainly Scytonema) (blackish layer)
	QUTB MONUMENTS	
xii)	Side wall of IInd entrance gate of Qutb Minar (The place of drinking water)	Scytonema
xiii)	Outer boundary of lawn in Qutb area	Gloeocapsa aeruginosa Scytonema burmanicum
xiv)	In the joints of wall of Quwwatu'I Islam Masjid	Scytonema

Table 3.3

Characters of Cyanophyceae Algae Found on the Surface of Stone from Different Monuments

	Algae	Characters
	Family Chroococcaceae	
1.	Microcystis pulverea (Wood)Forti	Colonies rounded to ellipsoidal, often many together, limits of colonial mucilage distinct, cells spherical, closely arranged, blue green, cell diameter = 2.2μ.
2.	Gloeocapsa aeruginosa (Carm)Kütz	Colonies spherical, cell light blue green, cell diameter without sheath = 2.7μ with sheath = 4.5μ
3.	Gloeocapsa livida (Carm) Kütz	Cells spherical, blue green, cell diameter, without sheath = 3.6μ with sheath = 6.2μ
4.	Gloeocapsa kuetzingiana (Nag)	Cells spherical, sheath unlamellated, yellow in colour, cell, without sheath = 3.6 μ broad with sheath = 5.4 μ broad
5.	Aphanothese pallida (Kütz) Rabenh	Thallus gelatinous, cells round to oval shaped, blue-green, sheath very distinct in the peripheral part of the thallus and diffluent in inner part cell 5.4 - 6μ broad 9.0 - 10.8μ long

Table 3.3 (Contd.)

	Family Oscillatoriaceae	Characters
6.	Oscillatoria jasorvensis Vouk	Filaments pale blue green, end cell rounded, cells nearly quadratic, 3.6μ broad 3.6μ long
7.	Oscillatoria pseudogeminata G. Schmid	Filaments pale blue-green, cells not constricted at the cross walls, sheath absent, end cell rounded, Cell quadratic, 1.8μ broad 1.8μ long
8.	Oscillatoria formosa Bory ex Gomont	Filaments blue green, slightly constructed at the cross walls, cells nearly quadratic 4.5-5.6μ broad 4.5-5.6μ long
9.	Oscillatoria schultzii Lemm.	Filaments dark green, distinctly constricted at the cross walls, end cell conical, cell 2.4μ broad 3.6μ long
10.	Lyngbya truncicola Ghose	Filaments straight, sheath unlamellated, at first hyaline and delicate and later firm and yellowish, blue green, granular, filament 14.4μ broad Trichome 12.8μ broad cell 3 μ long
11.	Lyngbya allorgei Fremy	Sheath very thin, colourless, trichome blue green, Trichome 3.6μ broad cell 7.2μ long
12.	Lyngbya martensiana Var. Calcarea Tilden.	Sheath colourless, trichome blue green Filament = 7.2μ broad Trichome = 5.4μ broad cell = 2.3μ long

Table 3.3 (Contd.)

		Characters
	Family Nostocaceae	
13.	Cylindrospermum musicola kützing ex Born. et Flah.	Trichome light blue green, cells quadratic 3.6μ broad, Heterocyst oblong 3.6μ broad and 5.4μ long, Vegetative form as spores are absent.
14.	Nostoc paludosum kützing ex Born. et Flah.	Thallus gelatinous, trichome pale blue-green, cells barral shaped, 3.6μ broad and 5.4μ long, Spores oval, 3.6μ broad and 7.2μ long.
	Family Scytonemataceae	
15.	Scytonema burmanicum Skuja	Filaments false branched-solitary, sheath lamellated, yellowish, cell blue green filament 17.2-18μ broad, trichome 8-11μ broad cell 5.4μ long, Heterocyst cylindrical, 12.6μ broad and 9.0μ long.
16.	Scytonema hofmanni Ag. ex Born. et Flah.	Filaments false branched, 10.8μ broad, sheath membranous, trichome 9μ broad, cell 7.2μ long, cell contents blue green, changed to yellowish in dried filaments.
17.	Tolypothrix byssoidea (Berk.) Kirchner	Filaments irregularly false branched, 14.4μ broad sheath thin and colourless, trichome 9μ broad, cells 4.5μ long, blue green contents of cells became yellowish showing the dried filaments, Heterocyst basel, 9.0μ broad and 7.2μ long.

Table 3.4

Algae and Moss Population Found On Different Stones

Family	Microbes	Substrate
CYANOPHYCEAE ALGAE		
Chroococcaceae	Microcystis pulverea	Marble
''	Gloeocapsa aeruginosa	Quartzite
''	Gloeocapsa livida	Sandstone
''	Gloeocapsa kuetzingiana	''
''	Aphanothese pallida	''
Oscillatoriaceae	Oscillatoria jasorvensis	''
''	Oscillatoria pseudogeminata	Sandstone, Marble
''	Oscillatoria formosa	Marble
''	Oscillatoria schultzii	''
''	Lyngbya truncicola	Sandstone and Marble
''	Lyngbya allorgei	Marble
''	Lyngbya martensiana	''
Nostocaceae	Cylindrospermum musicola	Sandstone
''	Nostoc paludosum	''
Scytonemataceae	Scytonema burmanicum	Quartzite
''	Scytonema hofmanni	Mortar Material
''	Tolypothrix byssoidea	Marble
BRYOPHYTES		
Ricciaceae	Riccia	Mortar and Quartzite
Funariaceae	Funaria	Mortar, Quartzite and Sandstone

generic names should be underlined

could be identified .

In the case of bryophytes, two types of plants, Riccia and funaria (Table 3.2, site no. ii, iii, xi) were abundantly found, having always a dried blackish layer of algae and other humus deposition beneath it. Moss often found on deteriorating structures, particularly on porous and humid zones (xi).

3.3.2 Diagrams of Algal Species Drawn by Camera Lucida

Figures 3.2 to 3.5 depict the diagrams of various species of Cyanophyceae, drawn by camera lucida under 100x15 magnification. The detailed description is given below :

3.3.2.1 Members of Chroococcaceae

Figure 3.2 (A-E) shows three members of Cyanophyceae algae belonging to family Chroococcaceae. Figures B, C and D represent three different species of Gloeocapsa.

3.3.2.1.1 Microcystis pulverea (Wood) Forti

Spherical cells (2.2µ diameter) of the species closely arranged in the form of rounded to ellipsoidal colonies (Fig. 3.2A), which were usually present in large numbers. Cells are of characteristic blue-green colour. The species of Microcystis was found in the dark green and brown layer around the boundaries of Central tank, of marble filled with water, in Jama Masjid (Viii). The species was present along with the other species of Oscillatoria.

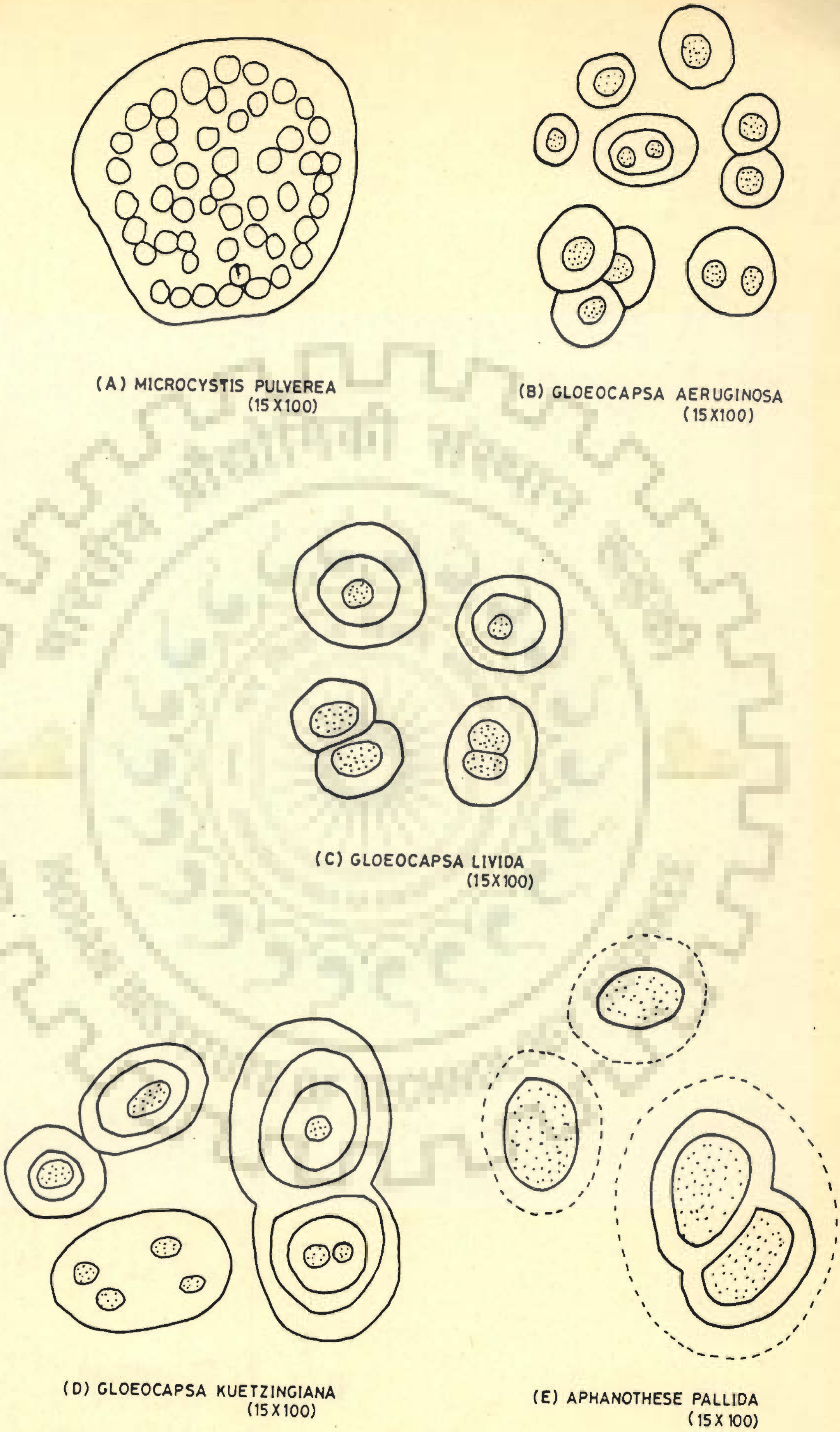


FIG. 3·2. MEMBERS OF CHROOCOCCACEAE

3.3.2.1.2 <u>Glosocapsa aeruginosa</u> (Carm.) Kiitz.

The spherical, blue green cells of the species were measured to be 2.7μ (without sheath) and 4.5μ broad (with sheath) (Fig. 3.2B). The species was found to be present in the green layer of outer boundary of the lawn in Qutb area (xiii).

3.3.2.1.3 <u>Gloeocapsa livida</u> (Carm.) Kiitz.

Spherical cells of the species were measured to be 3.6μ (without sheath) and 6.2μ (with sheath) (Fig. 3.2c). The sheath is light bluish and the contents of cells are also light blue green in colour. The species was present in the blackish layer grown on the side wall of Shahi-Hammam(ii) (Royal Swiming pool) in Red Fort.

3.3.2.1.4 <u>Gloeocapsa kuetzingiana</u> Nag

This species of Gloeocapsa was found to be present in the blackish layer developed on the surface of a deteriorated structure on the lawn near the Shahi-Hammam (iii). Cells were of 3.6μ size (without sheath) and 5.4μ (with sheath)(Fig.3.2D). Sheath of the cells is unlamellated and yellow in colour.

3.3.2.1.5 <u>Aphanothese pallida</u> (Kiitz) Rabenh

The thallus of the species was gelatinous, The blue green, oval cells were measured to be 5.4-6μ broad and 9.0 - 10.8μ long (Fig. 3.2E). Sheath around the cells is very distinct in the peripheral part of the thallus and diffluent in inner part. The species was found to present in dark green layer on the wall at the entrance of Red Fort (i) along with species of Oscillatoria.

3.3.2.2 Members of Oscillatoriaceae

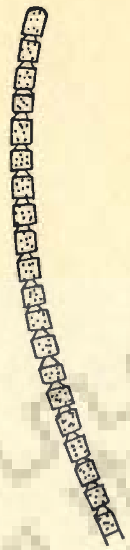
Figures 3.3 (A-G) show the different species of two members of Cyanophyceae belonging to family Oscillatoriaceae. Four species of Oscillatoria (Fig. 3.3 A-D) and three of Lyngbya (Fig. 3.3 E-G) were identified.

3.3.2.2.1 Oscillatoria pseudogeminata G. Schmid

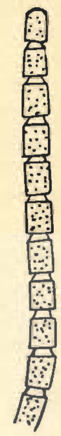
The cells of straight, pale blue-green filament of this species are quadratic, generally slightly less than 1.8μ in size, end cell rounded (Fig. 3.3 A). The species was most commonly found alongwith Aphanothese, Microcystis, Lyngbya and also with other three species of Oscillatoria, present in the dark green layer developed on the wall at the entrance of Red Fort (i), around the boundaries of Central space in Moti-Masjid (Red Fort) (vi) and of central tank in Jama-masjid(viii) and in the joints of staircases of entrance of Jama-masjid(ix).

3.3.2.2.2 Oscillatoria schultzii Lemm.

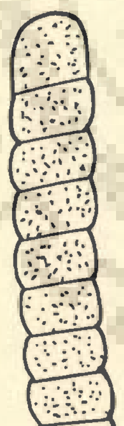
The cells of this species of Oscillatoria are nearly barral shaped, generally 2.4μ diameter and 3.6μ long (Fig. 3.3B), the pale blue-green trichome is constricted at the cross walls. This species was found to be present along with Microcystis and also other species of Oscillatoria, in the dark green layer grown around the boundaries of central tank, filled with water, in Jama-masjid (viii).



(A) OSCILLATORIA PSEUDOGEMINATA
(15 X 100)



(B) OSCILLATORIA SCHULTZII
(15 X 100)



(C) OSCILLATORIA FORMOSA
(15 X 100)

(D) OSCILLATORIA JASORVENSIS
(15 X 100)

FIG.3·3(I) MEMBERS OF OSCILLATORIACEAE

3.3.2.2.3 Oscillatoria formosa Bory ex Gomont

The filament of this species of Oscillatoria is broad, cells are almost quadratic (4.5-5.6μ), trichome is slightly constricted at the cross walls, end cell is nearly obtuse (Fig. 3.3C). This species was found to present in the samples collected from the boundaries of central tank in Jama-masjid (viii) along with Oscillatoria formosa and Microcystis.

3.3.2.2.4 Oscillatoria jasorvensis Vouk

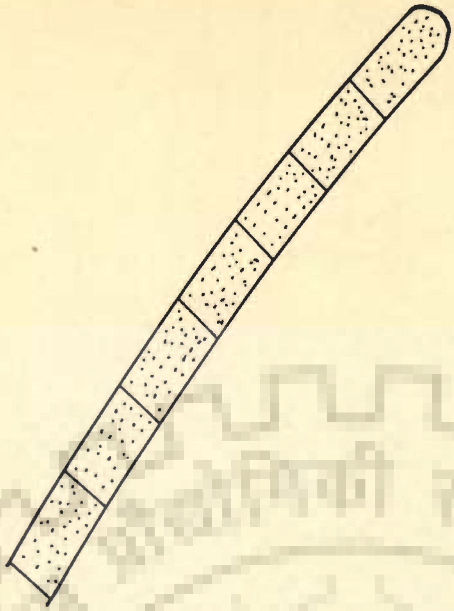
The pale blue green trichome has quadratic cells of 3.6μ size with terminal cell of round shape (Fig. 3.3D). The species was found to be present in dark green layer collected from the mortar joints of staircases of entrance of Jama-masjid (ix) along with Lyngbya and Oscillatoria pseudogeminata.

3.3.2.2.5 Lyngbya allorgei Fremy

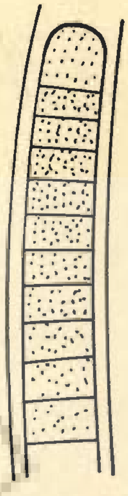
Blue green trichome and cells of the species of Lyngbya were measured to be 3.6μ in diameter and 4.2μ long, (Fig. 3.3E). As observed under microscope the sheath appeared to be very thin and colourless. This species was present in the dark green layer around the boundaries of central space in Moti-masjid (Red Fort) (vi) along with other species of Lyngbya and Oscillatoria pseudogeminata.

3.3.2.2.6 Lyngbya martensiana Var. Calcarea Tilden

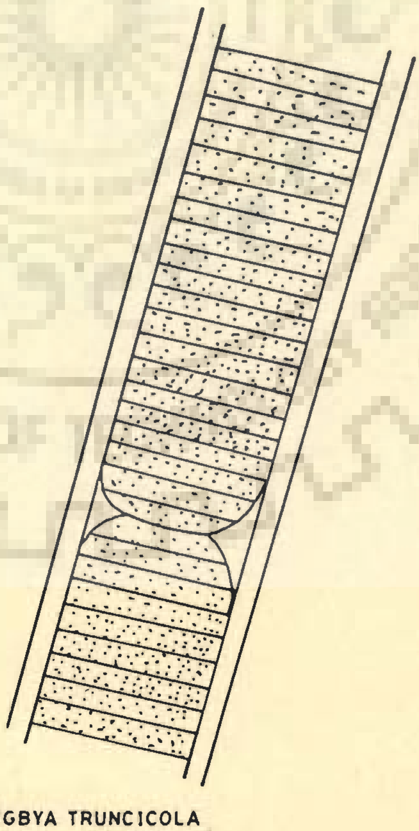
As the name indicates, this variety of Lyngbya was found from calcareous substrate around the boundaries of



(E) LYNGBYA ALLORGEI
(15×100)



(F) LYNGBYA MARTENSIANA VAR. CALCAREA
(15×100)



(G) LYNGBYA TRUNCICOLA
(15×100)

FIG.3·3(2) MEMBERS OF OSCILLATORIACEAE

central space in Moti-masjid (Red Fort) (vi) along with other species of Lyngbya and Oscillatoria pseudogeminata. Bluish green trichome is of 5.4μ diameter, filament (with sheath) 7.2μ diameter, cells 2.3μ long (Fig. 3.3F), sheath colourless.

3.3.2.2.7 Lyngbya truncicola Ghose

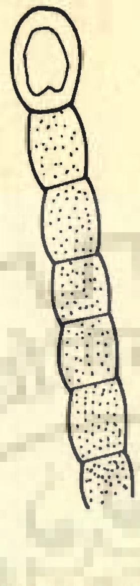
The slides show both young and matured filaments of this species. Filaments were measured to be 14.4μ broad, unlamellated sheath hyaline and delicate in young filaments and became firm and yellowish in mature filaments, blue-green trichome of 12.8μ diameter and cells are 3μ long, contents of cells are granular (Fig. 3.3G). This species was found to be present in the samples collected from the blackish layer grown on the wall of Shahi-Hammam (Redfort)(ii), from the carvings of the wall in Diwan-I-Khas (Red Fort)(v) and from the mortar joints in the staircases of entrance of Jama-masjid (ix).

3.3.2.3 Members of Nostocaceae

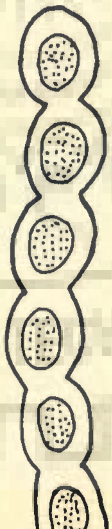
Figures 3.4 (A-B) show two genra of Cyanophyceae belonging to family Nostocaceae.

3.3.2.3.1 Cylindrospermum musicola Kiitzing ex Born at Flah.

The cells of the species were observed to be light blue green in colour, quadratic, almost 3.6μ in size, oblong heterocyst present at the top of filament is of 3.6μ diameter



(A) CYLINDROSPERMUM MUSICOLA
(15×100)



(B) SPORES OF NOSTOC PALUDOSUM
(15×100)

FIG.3·4. MEMBERS OF NOSTOCACEAE

and 5.6µ long. The species was in vegetative form as the spores were absent (Fig. 3.4A). It was found in light green layer collected from the mortar joints of the staircases of the entrance of Jama-masjid (ix).

3.3.2.3.2 Nostoc paludosum Kiitzing ex Born et Flah.

Thallus of Nostoc is gelatinous. Barrel shaped cells were measured of 3.6µ diameter and 5.4µ long. The species was in reproductive stage showing oval spores, larger than vegetative cells, (3,6µ diameter and 7.2µ long) (Fig. 3.4B). It was found in the greenish layer grown in the horizontal and vertical joints in the wall of Rang Mahal (Red Fort)(iv).

3.3.2.4 Members of Scytonemataceae

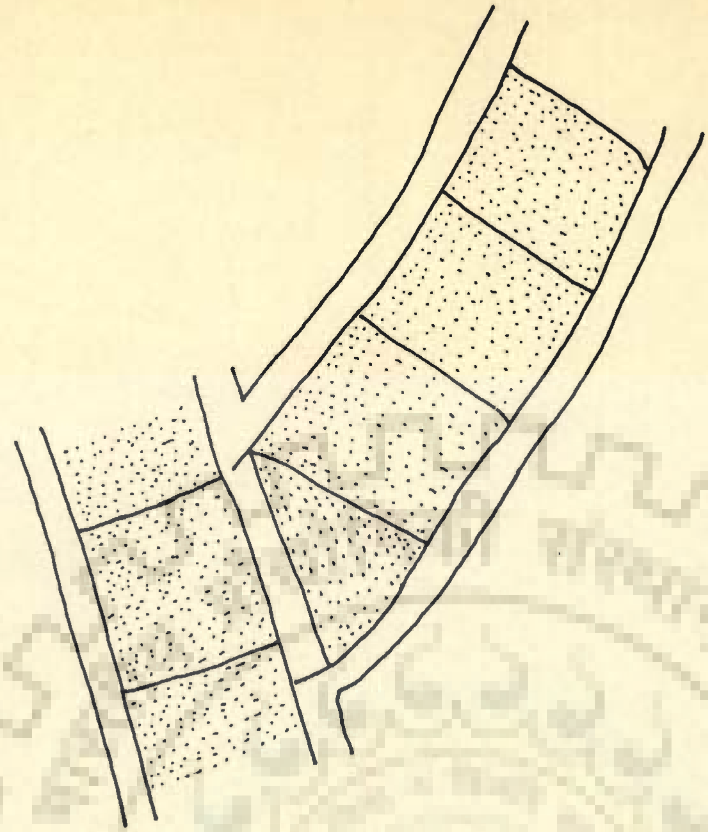
Figures 3.5 (A-B) show two genera of Cyanophyceae algae belonging to family Scvtonemataceae.

3.3.2.4.1 Scytonema hofmanni Ag. ex Born. et Flah.

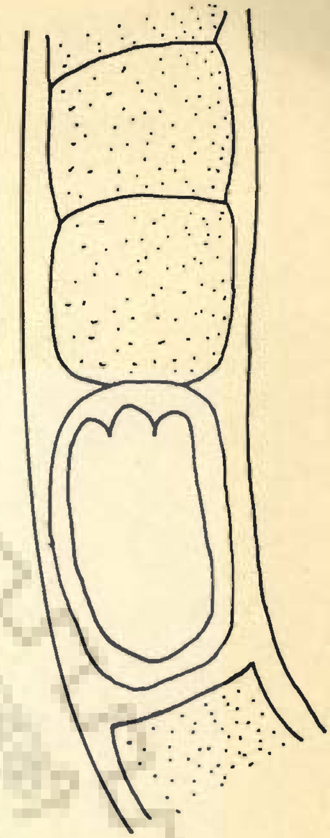
Filaments of Scytonema show false branching, sheath membranaceous, filament of 10.8µ diameter, trichome of 9µ and blue green in colour, slightly dried filaments show yellowish colour, cells unequal in length, generally 7.2µ long (Fig. 3.5A). The species was found from the abundant growth on the walls of Kotla Firoj Shah (x).

3.3.2.4.2 Scytonema burmanicum Skuja

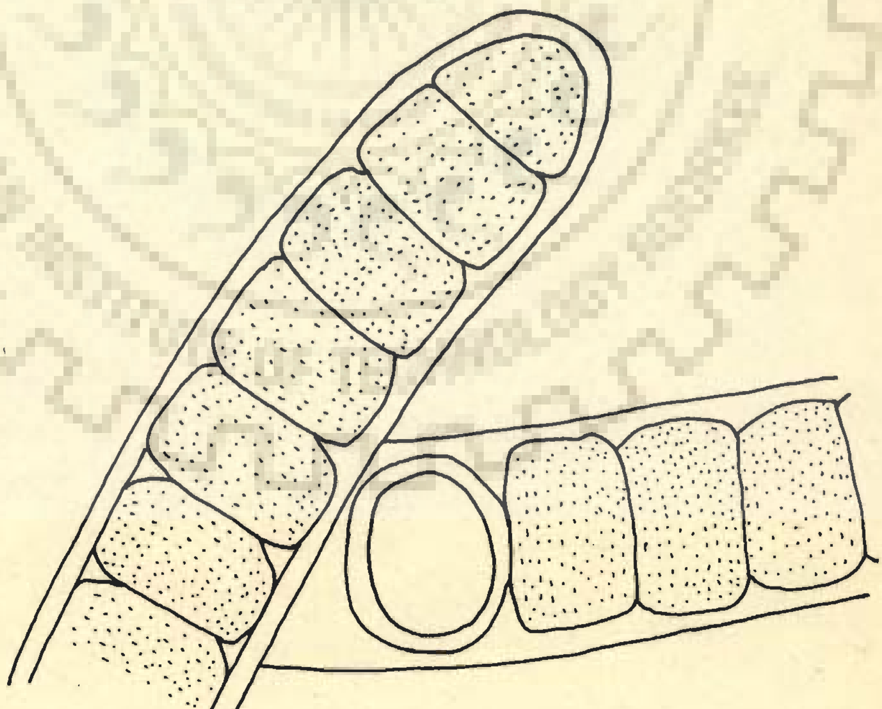
Filaments of Scytonema show false branching, sheath lamellated and yellow in colour. Filaments were measured to



(A) SCYTONEMA HOFMANNI
(15 × 100)



(B) SCYTONEMA BURMANICUM
(15 × 100)



(C) TOLYPOTHRIX BYSSOIDEA
(15 × 100)

FIG.3·5. MEMBERS OF SCYTONEMATACEAE

be 17.2 - 18μ broad, trichome (without sheath) of 8-11μ diameter and the cells 5.4μ long. The contents of cell were blue green, however dried filaments were also present showing yellowish contents. Heterocyst present was found to be of 12.6μ diameter and 9.0μ long (Fig. 3.5B). It was developed on the outer boundary of lawn in Qutb area (xiii).

3.3.2.4.3 *Tolypothrix byssoidea* (Berk.) Kirchner

Filaments of *Tolypothrix* show irregular false branching, 14.4μ broad, sheath thin, trichome 9.0μ broad, cell 4.5μ long, yellowish contents of cells show dried filaments, heterocyst 9.0μ broad and 7.2μ long (Fig. 3.5C). It was found from the carvings of the wall in Diwan-I-Khas (Red Fort) (V) with *Lyngbya truncicola*.

Photomicrographs of different algal species are shown in plates 3.1 to 3.4.

Fig. 3.6 shows the hand sketch diagrams of two members of bryophytes, Riccia and Funaria. Riccia has rosette shaped structure and commonly occurs on moist shady places, damp walls, rocks and moist tree trunks. Funaria plant is radially symmetrical, differentiated into stem and leaves and commonly occurs on damp walls, crevices, moist soil and rocks in the form of close tufts.

3.3.3 Prevention of Microbial Growth

The results of the growth of microbial samples in culture medium with and without preservatives are shown in

FIG.3·6. MEMBERS OF BRYOPHYTES

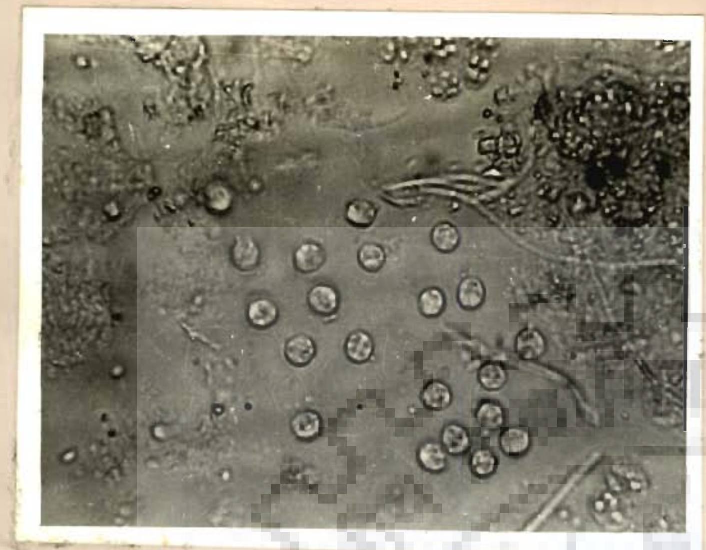
Photomicrographs (3.1) (a to d) showing the different members belonging to family Chroococcaceae

Plate 3.1 (a) shows clear round shaped colonies of Microcystis pulverea along with filamentous member, Oscillatoria, of family Oscillatoria. The extra matrial appeared in the plate shows the dusty material present in the slide (10x40)

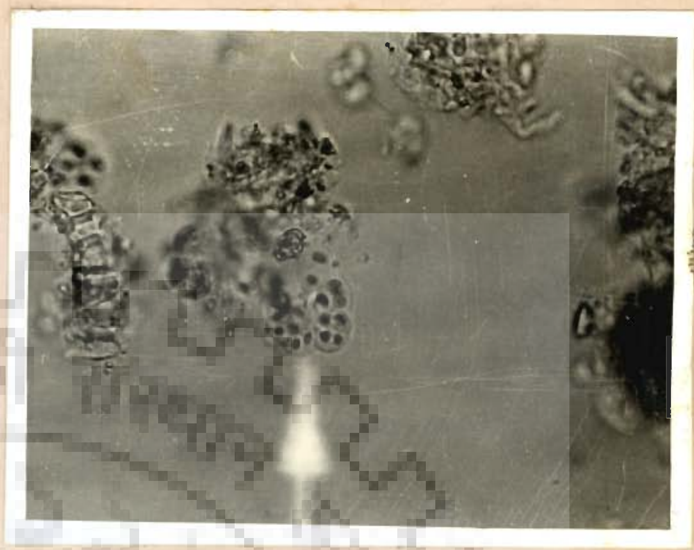
Plate 3.1 (b) arrow shows the round shaped colonies of Gloeocapsa kuetzingiana, the remaining colonies are not very much clear in the plate (10x40)

Plate 3.1 (c) shows the colonial mass of Gloeocapsa livida, however, the photomicrograph is not clear as the plate does not show colonies of the member clearly. (10x40)

Plate 3.1 (d) shows clear oval shaped cells of Aphanothese pallida, few round shaped young cells are also present, along with filamentous form of Oscillatoria pseudogeminata which are, however, not clearly visible in the plate (10x40)



(a) *Microcystis pulverea* along with Oscillatoria (10x40)



(b) *Gloeocapsa kuetzingiana* (10x40)

(c) Colonial mass of *Gloeocapsa lividа* (10x40)

(d) *Aphanothese pallida* (10x40)

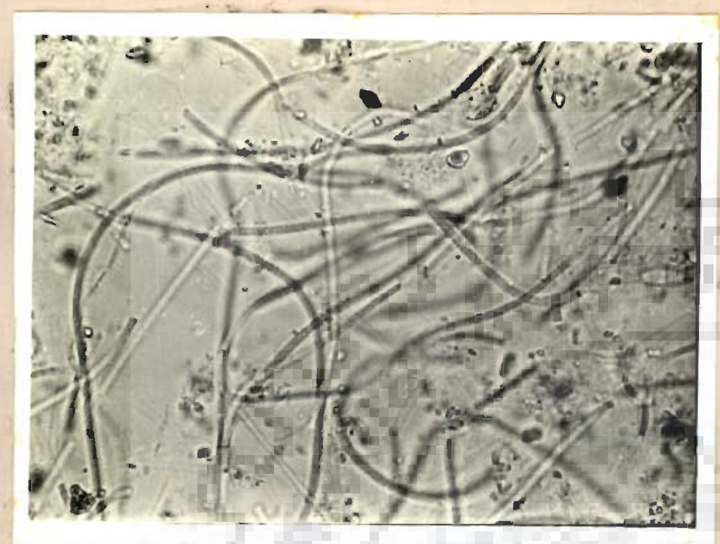
PLATE 3.1

Photomicrographs 3.2 (a-c) showing different members belonging to family *Oscillatoria* :

Plate 3.2 (a) shows the filaments of *Oscillatoria schultzii* (10x40)

Plate 3.2 (b) shows the broader filaments of *Oscillatoria formosa* along with less broad filaments of *Oscillatoria schultzii*. The plate clearly shows the quadratic cells of the filaments, some dusty material is also present in the slide (10x40).

Plate 3.2 (c) shows a clear broad filament of *Lyngbya trucicola* (10x40).



(a) Oscillatoria schultzii
(10x40)

(b) Oscillatoria formosa
(10x40)

(c) Lyngbya truncicola
(10x40)

PLATE 3.2

Photomicrographs 3.3 (a-d) showing two members belonging to family Nostocaceae.

Plate 3.3 (a) shows filaments of _Cylindrospermum musicola_, the cells are nearly quadratic, vegetative in form, as the spores are absent (10x40)

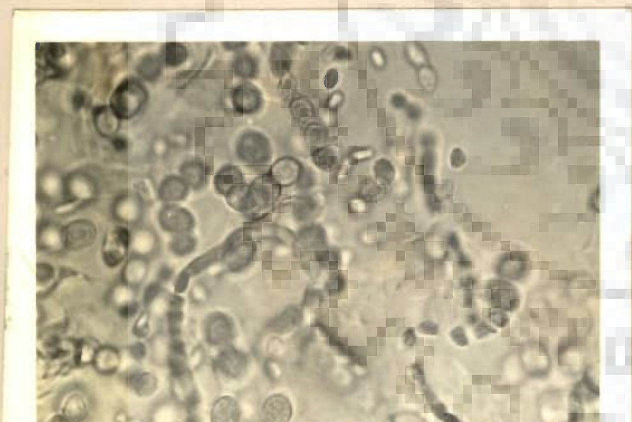
Plate 3.3 (b) shows one filament of _Cylindrospermum musicola_, apical cell shows oblong heterocyst (10x125).

Plate 3.3 (c) shows the cells and spores of _Nostoc paludosum_, th sample is in reproductive stage (10x40).

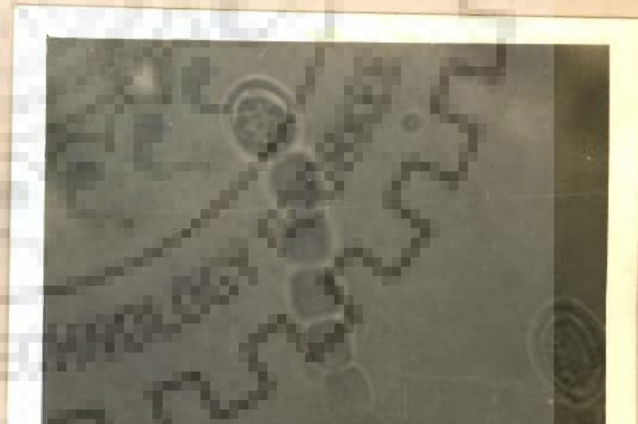
Plate 3.3 (d) shows one filament showing of barral shaped spores of _Nostoc paludosum_ (10x125).

(a) Cylindrospermum musicola
(10x40)

(b) Cylindrospermum musicola
(10x125)



(c) Nostoc paludosum
(10x40)



(d) Nostoc paludosum
(10x125)

PLATE 3.3

Photomicrographs 3.4 (a-b) showing two members belonging to family Scytonemataceae.

Plate 3:4(a) shows the filaments of Scytonema hofmanni (10x40)

Plate 3.4(b) shows one filament of Scytonema burmanicum, arrow shows the cylindrical heterocyst present (10x40)

Plate 3.4(c) shows the spore of Alternaria along with some dusty material.

(a) *Scytonema hofmannii* (10x40)

(b) *Scytonema burmanicum* showing heterocyst(10x40)

(c) Spore of fungus, *Alternaria* (10x40)

PLATE 3.4

plate 3.5. A rough estimation of these growths is given in Table 3.5.

Table 3.5

Sl. No.	Sample	Growth
1.	Microbial Sample + Culture medium	+++
2.	Microbial Sample + Barium Hydroxide Solution + Culture medium	-
3.	Microbial Sample + PMMA + Culture medium	+
4.	Microbial Sample + Silicone Resin + Culture medium	-

+ Small growth, ++ medium growth, +++ good growth

- no growth

The results obtained clearly showed that barium hydroxide solution, PMMA and silicone resin retarded the biological growth. These results are in agreement with those reported by Alessandrini et. al. (1978) that acrylic silicone resin and epoxy aliphatic resin retarded the growth of algae to a considerable extent.

3.4 CONCLUSION

From the above study it was found that Cyanophyceae algae was present at every site of collection. Presence of accessory pigments such as phycobilin in Cyanophyceae which allow them to survive even in low light conditions explains the wide presence of this class of algae (Techneco, 1977).

Plate 3.5 :
Growth of Micro-Organisms in Culture Medium with and without Preservatives

1: In Culture Medium
2: With Barium Hydroxide Solution
3: With PMMA
4: With Silicone Resin

The different genera identified in the study had also been identified previously by other workers e.g. species of Microcystis, Gloeocapsa, Oscillatoria and Lyngbya had also been identified from Agra monuments both of marble and red sandstone (Techneco, 1977), presence of Scytonema and Nostoc have been mentioned on Borobudur temple (Samidi, 1981) and Aphanothese, Gloeocapsa, Oscillatoria, Nostoc and Scytonema had also been identified (Grossin, 1978).

Among 17 species of Cyanophyceae identified, two members were found to be substrate-specific in nature, Microcystis pulverea and Lyngbya martensiana Var. Calcarea which are known to occur on calcareous substrate.

Table 3.6 indicates the presence of organic acids secreted by different microorganisms which degrade the stone substrate. However, no acid was reported secreted by algae. Though Cyanophyceae algae were found to inhabit calcareous substrate (cal:rocks, shells and corals) as epilithic and endolithic forms. The entire plant or parts of plant perforate into the calcareous substratum by the direct action of a solvent excreted by algae. (Desikachary 1959; Fritsch, 1959) It is not certain how penetration is effected although secretion of Oxalic acid is suspected (Fritsch, 1959). Many Cyanophyceae have the capacity to precipitate appreciable quantities of lime (Glock, 1923), which may in certain instances lead to the production of extensive deposition. Following genera are known to have this capacity (Pia, 1934) : Gloeocapsa, Aphanothese, Oscillatoria, Lyngbya, Scytonema, Tolypothrix.

Table 3.6

Secretion of Acids by Micro-Organisms and their action on Stones

Microorganism	Acid Identified	Type of Stone	Possible Action
Fungi	Oxalic Acid Citric Acid Gluconic Acid Acetic Acid Lactic Acid	Sandstone	Decompose felspar mineral into Kaolin.
Lichen	Oxalic Acid	Calcareous sandstone, marble and limestone	Dissolve calcareous material as calcium oxalate, decompose felsper mineral into biotite and take alkali metals from the rock.
Algae	Unidentified	Sandstone, marble	Boring capability for calcareous substrate by the secretion of solvent. Ability to fix atmospheric N_2 to produce nitrogen compounds which are used by nitrobacteria causing further corrosive attack. Retain moisture and prepare ground for other microbes to fluorish.
Moss	Unidentified	Sandstone	Develop only on deposition of humus which further permits to develop higher plants.

Boring capability of Cyanophyceae algae was also reported (Krumbein, 1978), but the kind of acid and the exact mechanism of degradation are not known (Friedman, 1978). Besides the degrading effect, Cyanophyceae work as a ground for other microbes by retaining the humidity (Richardson 1980), fixing the atmospheric nitrogen (Allison 1930; Techneco 1977) and also work as a source of organic matter for heterotrophs by liberating 5-50% of fixed carbon in the atmosphere (Karavaiko, 1978).

Mosses exert mechanical pressure on the rock as their rhizoids penetrate inside the rock following the system of vesicules and sometimes breaking the wall between them to a considerable extent. The presence of moss on stone surfaces further permits to develop higher plants.

Thus biological study clearly indicates that the growth of micro-organisms on the stone monuments can bring following types of important alterations in monuments :

(1) Morphological : due to the presence of organisms which, leaving aside any metabolic activity, can alter the aesthetic properties.

(2) Mechanical : due to physical phenomenon of penetration and due to consequent effect (e.g. expansion in the freezing - melting cycles of water retained by their thalli).

(3) Chemical : due to the attack of organisms, directly, for the source of nutritive elements, and by their metabolic products causing physical corrosion and chemical changes in the monument.

The preservatives barium hydroxide solution, PMMA and silicone resin found suitable to enhance durability characteristics of the stones have also been found to retard the biological growth over the stones.

CHAPTER IV

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF MAKRANA MARBLE

CHAPTER IV

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF MAKRANA MARBLE

4.1 INTRODUCTION

Marble is a metamorphic rock formed by the recrystallisation of limestone under the action of intense heat and pressure below the earth's crust. It is one of the most durable and hard building stone consisting mainly of calcite or dolomite or mixture of both with some other accessory constituents. The colour of the marble may be white, pink, red, green, yellow and black. In India good varieties of marble deposits are known to occur in Rajasthan, Haryana, Kashmir, Gujarat and in many parts of the southern India.

Marble is commonly used as blocks, slabs and tiles in temples and commercial buildings. Coloured marbles are used as ornamental stones. Makrana marble has been most widely used in the construction of our important historical buildings and monuments e.g. Taj Mahal, Red Fort, Agra Fort, Akbar Tomb, Biwi-ka-Makbara etc. which are now in various stages of deterioration. Several workers (Lal. 1978; Gauri, 1970, 1978) have tried to find out the causes of decay and suggested suitable remedial measures to preserve these famous old monuments. However, so far no definite preservative has been found for marble suitable under different environmental conditions. In view of this the present systematic study on Makrana marble has been taken up.

The present chapter describes the physico-chemical, mineralogical, weathering and durability characteristics of Makrana marble and their inter-relationship with each other. The effectiveness of different preservatives namely barium hydroxide, polymethylmethacrylate (PMMA), styrene and silicone resin have been studied under different simulated environmental conditions.

4.2 EXPERIMENTAL PROCEDURES

Marble samples collected from the quarries (Makrana) were evaluated and subjected to different tests. The durability behaviour of the samples treated with barium hydroxide (8 percent), Styrene, PMMA (5 and 10 percent) and silicone resin (25 percent) was also studied under different tests. The details of the experimental procedures followed are described in Chapter II.

4.3 RESULTS

4.3.1 Physico-Chemical Characteristics

Physical characteristics of fresh marble samples like water absorption, porosity, specific gravity, density and compressive strength are given in Table 4.1. Water absorption, specific gravity and hardness values confirm the requirements laid down in the relevant specification for Marble (IS:1130).

The chemical analysis data given in Table 4.1 indicates that the Makrana marble sample consists mainly of calcium carbonate with minor amounts of magnesium carbonate.

Table 4.1

Physico-Chemical Characteristics of Makrana Marble Samples

Physical characteristics	Average Experimental values
Water Absorption (% by weight)	0.080
Porosity (% by volume)	0.23
True Specific Gravity	2.92
Apparent Specific Gravity	2.88
Real Density (gm/cm^3)	2.88
Bulk Density (gm/cm^3)	2.88
Compressive Strength (kg/cm^2)	1278
Hardness	3.5
Chemical Analysis	
Loss of Ignition (percent)	44.31 ?
Silica (SiO_2) (percent)	Nil
Iron Oxide (Fe_2O_3) (percent)	Nil
Aluminium Oxide (Al_2O_3) (percent)	Nil
Calcium Oxide (CaO) (percent)	53.60
Magnesium Oxide (MgO) (percent)	2.05

4.3.2 Mineralogical Characteristics

The megascopic characters of the stone show that it is a hard, compact, coarsely crystalline rock free from alteration product. Thin sections under microscope show typical saccoroidal texture. It consists mainly of calcite grains varying in size from medium to coarse grains. The calcite in most cases interlock each other with mica flakes occasionally present between the grains. The rock is otherwise free from impurities and does not show any crack or microcracks (Plate 4.1).

4.3.3 Weathering Test

The water absorption, porosity and weight loss characteristics of untreated marble during the weathering test cycles are shown in Table 4.2. These values progressively increased with the test cycles i.e. water absorption increased from 0.075 to 0.185 and porosity from 0.22 to 0.52 percent after 100 cycles. The weight loss was found to be 0.098 percent after 100 cycles of the test.

4.3.4 Durability Test

Durability studies carried out on untreated marble samples after subjecting them to different durability test conditions 1,2 and 3 (Table 2.2) showed the extent of variations in the water absorption, porosity and weight loss values of the samples (Table 4.3). These values at the disintegration point (32 cycles) under test condition (1) were found to be 0.25, 0.72 and 0.22 per cent respectively which

Photomicrographs showing different stages of Makrana marble under durability test :

Plate (4.1) Fresh marble showing well developed calcite grains exhibiting polysynthetic twinning and generally free from cracks and alteration products (X100)

Plate (4.2) Marble after 20 cycles of durability test showing the development of the micro-cracks and slight reduction of the size of calcite grains (X100)

Plate (4.3) Marble after the durability test showing considerable change in the shape and sizes of calcite grains (X100)

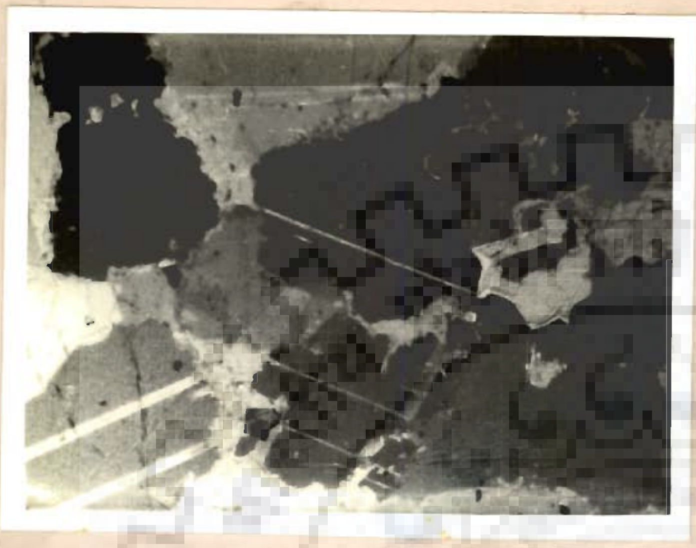


Plate 4.1: Fresh Makrana Marble x100

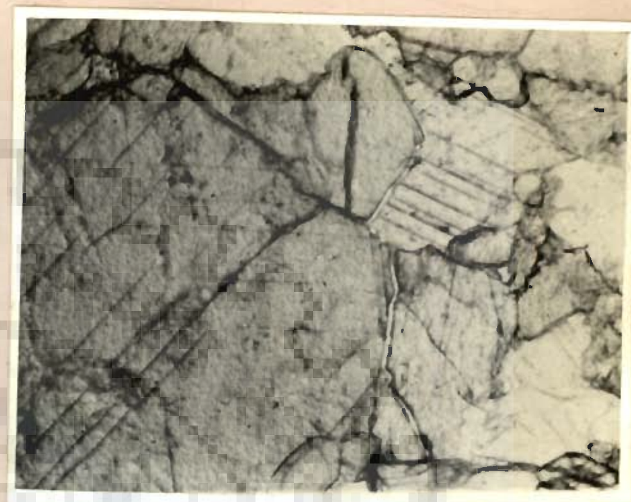


Plate 4.2: Marble after 20 cycles of Durability Test x100

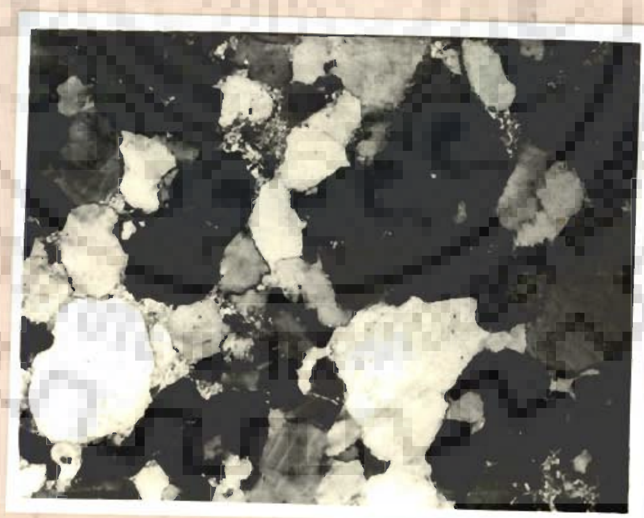


Plate 4.3: Marble after Durability Test x100

Table 4.2

Variation in Physical Properties of Marble Under Weathering Test

No. of Cycles	Water Absorption (%)	Porosity (%)	Weight loss (%)
Initial	.075	.22	-
10	.060	.17	.015
20	.067	.19	.023
30	.087	.25	.034
40	.090	.26	.034
50	.106	.29	.036
60	.108	.33	.049
70	.134	.39	.059
80	.136	.41	.073
90	.161	.45	.086
100	.185	.52	.098

Table 4.3

Variation in Physical Properties of Marble Under Different Durability Test Conditions

No. of Cycle	Durability Test Conditions								
	(1) Water Absorption (%)	(2)	(3)	(1) Porosity (%)	(2)	(3)	(1) Weight loss (%)	(2)	(3)
Initial	.093	.086	.090	.26	.25	.26	–	–	–
10	.112	.103	.095	.32	.29	.27	.075	.052	.051
20	.137	.129	.095	.40	.37	.27	.10	.069	.062
30	.195	.221	.096	.61	.64	.275	.17	.19	.066
32	.252*	–	–	.72*	–	–	.22*	–	–
38	–	.560**	–	–	1.60**	–	–	.91**	–
40	.60**	–	.097	1.75**	–	.275	1.47**	–	.074
50	–	–	.098	–	–	.28	–	–	.13
60	–	–	.102	–	–	.29	–	–	.14
70	–	–	.103	–	–	.29	–	–	.19
80	–	–	.105	–	–	.30	–	–	.21
90	–	–	.112	–	–	.32	–	–	.28
100	–	–	.122	–	–	.35	–	–	.29

*Appearance of crack **Samples disintegrated further increased to 0.60, 1.75 and 1.47 per cent after 40 cycles (Plate 4.4). Under test condition (2) these values were 0.56, 1.60 and 0.91 per cent after disintegration (38 cycles) (Plate 4.5), however, under test condition (3) these values were found to be only 0.122, 0.35 and 0.29 per cent respectively even after 100 cycles of the test without showing any sign of disintegration (Plate 4.6).

The water absorption, porosity and weight loss values of marble samples treated with different preservatives (under vacuum) during the durability test condition (3) are given in Tables 4.4, 4.5 and 4.6. The marble samples treated with $Ba(OH)_2$ failed after 87 cycles of the durability test having 0.14, 0.40 and 1.48 per cent water absorption, porosity and weight loss values respectively, while the samples treated with PMMA,styrene and silicone resin passed 100 cycles of the durability test without showing any sign of disintegration or cracking (Plates 4.7 to 4.15).

By the treatment with 5 per cent PMMA the water absorption and porosity values initially decreased from 0.087 to 0.071 and 0.25 to 0.21 per cent respectively. After 100 cycles of the test these values increased to 0.120 and 0.35 per cent respectively. The samples coated by brush showed the decrease of water absorption from 0.082 to 0.072 and porosity from 0.25 to 0.23 per cent which were found to increase to 0.14 and 0.40 per cent respectively after 100 cycles of the test. The samples treated under vacuum show the weight loss value 0.15 per cent whereas samples treated by brush have 0.44 per cent weight loss after 100 cycles (Table 4.7).

Table 4.4

Variation in Water Absorption values of Treated Marble under Durability Test Condition (3)

Treatment	Barium Hydroxide (8%)	PMMA (5%)	PMMA (10%)	Styrene	Silicone Resin (25%)
No. of cycles	Water Absorption (%)				
Initial	.080	.087	.083	.071	.070
After coating	.065	.071	.062	.054	.051
10	.069	.088	.081	.067	.052
20	.075	.091	.084	.070	.052
30	.080	.094	.088	.075	.053
40	.083	.097	.091	.079	.053
50	.090	.102	.095	.084	.054
60	.100	.105	.100	.089	.054
70	.113	.109	.102	.095	.055
80	.121	.112	.106	.099	.055
87	.140*	-	-	-	-
90	-	.116	.111	.102	.056
100	-	.120	.115	.108	.056

*Samples disintegrated

Table 4.5

Variation in Porosity values of Treated Marble under Durability Test Condition (3)

Treatment	Barium Hydroxide (8%)	PMMA (5%)	PMMA (10%)	Styrene	Silicone Resin (25%)
No. of cycles		Porosity (%)			
Initial	.24	.25	.24	.20	.26
After coating	.18	.21	.17	.15	.140
10	.20	.25	.23	.19	.140
20	.22	.26	.24	.20	.142
30	.23	.27	.25	.21	.144
40	.24	.28	.25	.22	.148
50	.26	.29	.27	.24	.150
60	.29	.30	.28	.24	.150
70	.33	.31	.29	.27	.154
80	.35	.32	.30	.28	.156
87	.40*	-	-	-	-
90	-	.34	.31	.29	.158
100	-	.35	.32	.30	.160

*Samples disintegrated

Table 4.6

Variation in Weight Loss Values of Treated Marble under Durability Test Condition (3)

Treatment	Barium Hydroxide (8 %)	PMMA (5%)	PMMA (10%)	Styrene	Silicone (25%)
No. of Cycles	Weight loss (%)				
10	Nil	.029	.080	.016	Insignificant
20	''	.034	.10	.017	''
30	.011	.042	.10	.10	''
40	.014	.065	.13	.025	''
50	.047	.073	.15	.035	''
60	.42	.080	.17	.047	''
70	.56	.087	.18	.049	''
80	1.00	.10	.22	.059	''
87	1.48*	–	–	–	''
90	–	.12	.23	.062	''
100	–	.15	.25	.089	''

*Samples disintegrated

Table 4.7

Durability Behaviour of Makrana Marble

Untreated/ Treated	Initial Water Absorption (%)	Initial Porosity (%)	After coating Water Absorption (%)	After coating Porosity (%)	Disintegration cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)	Rate of Decay (wt.loss/ cycle)
Untreated (1)	.093	.26	-	-	32	.252	.72	.22	.0068
			-	-	40	.60	1.75	1.47	.037
(2)	.086	.25	-	-	38	.56	1.60	.91	.028
(3)	.090	.26	-	-	100**	.12	.35	.29	.0029
Treated with Barium hydroxide (8%)									
Under Vacuum	.080	.24	.065	.18	87*	.14	.40	1.48	.017
PMMA (5%)									
Under Vacuum	.087	.25	.071	.21	100**	.12	.35	.15	.0015
By Brushing	.082	.25	.072	.23	100**	.14	.40	.44	.0044
PMMA (10%)									
Under Vacuum	.083	.24	.062	.17	100**	.115	.32	.25	.0025
By Brushing	.078	.23	.069	.21	100**	.12	.37	.61	.0061
Styrene									
Under Vacuum	.071	.20	.054	.15	100**	.108	.30	.089	.00089
By Brushing	.071	.21	.061	.17	100**	.183	.51	.096	.00096
Silicone Resin (25%)									
Under Vacuum	.070	.26	.051	.14	100**	.056	.16	.003	.00003
By Brushing	.078	.23	.064	.18	100**	.103	.29	.007	.00007

*Samples disintegrated **Samples not disintegrated

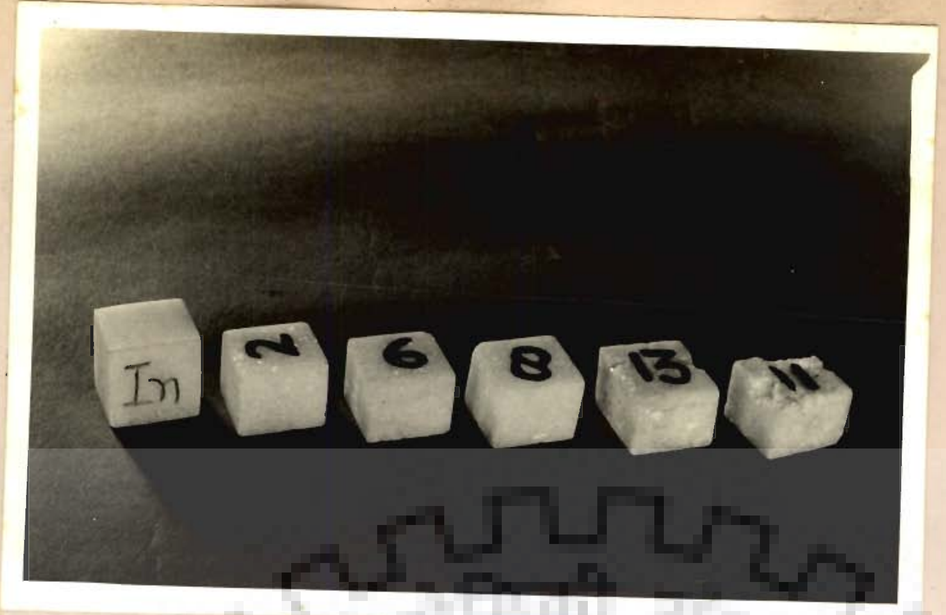


Plate 4.4: Durability Behaviour of
Marble Under Test Condition (1)

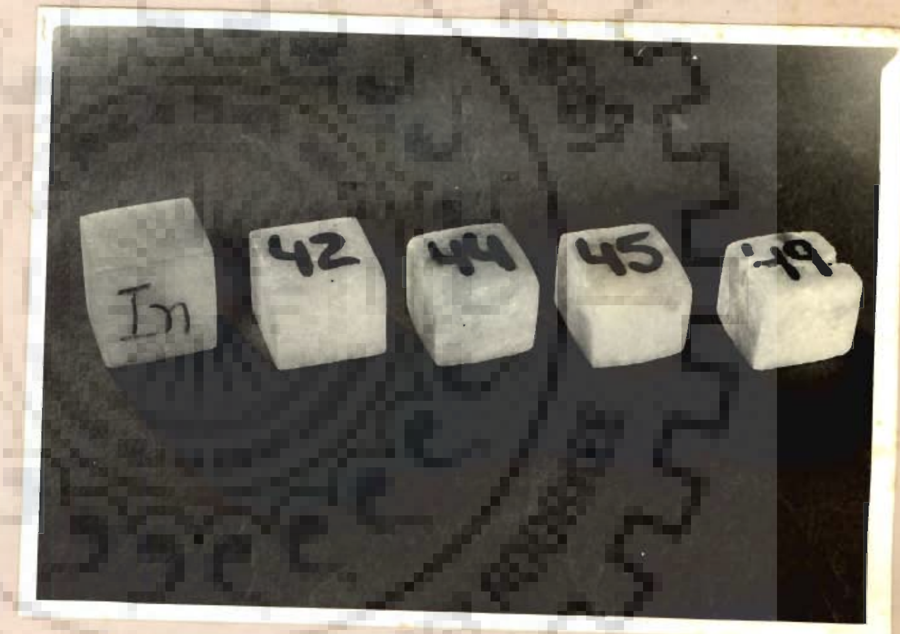


Plate 4.5: Durability Behaviour of
Marble Under Test Condition (2)

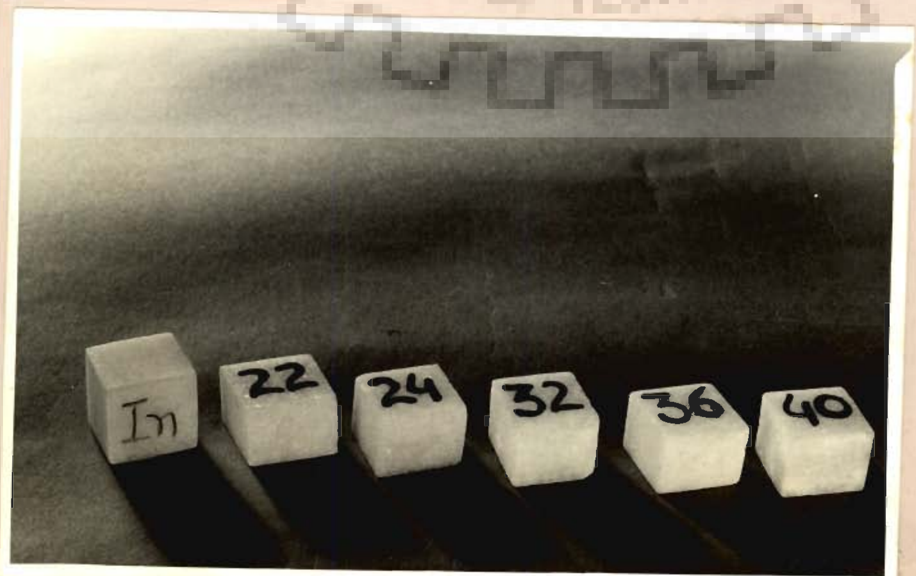


Plate 4.6: Durability Behaviour of Marble

Marble Samples Treated Under Vacuum

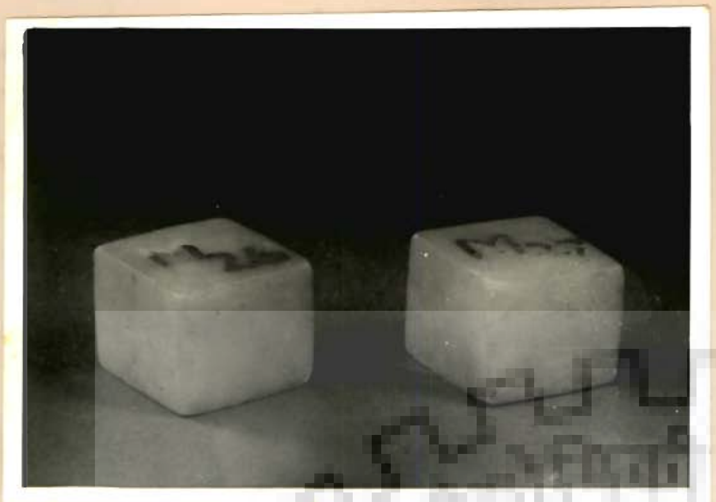


Plate 4.7: With Silicone Resin after 100 cycles

Plate 4.8: With Styrene after 100 cycles

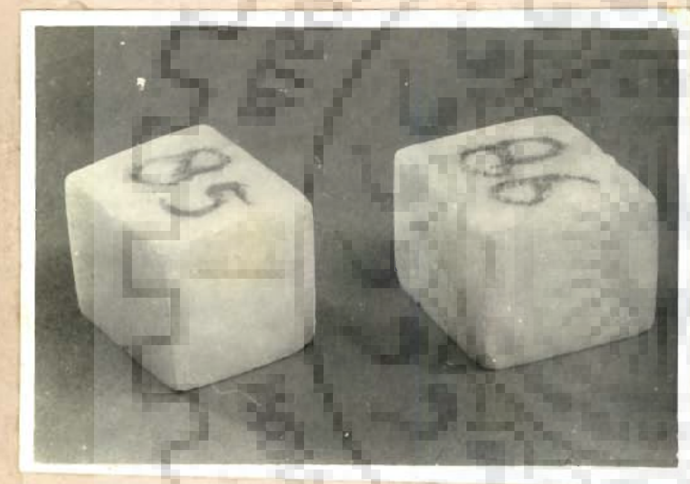


Plate 4.9: With PMMA (5%) after 100 cycles

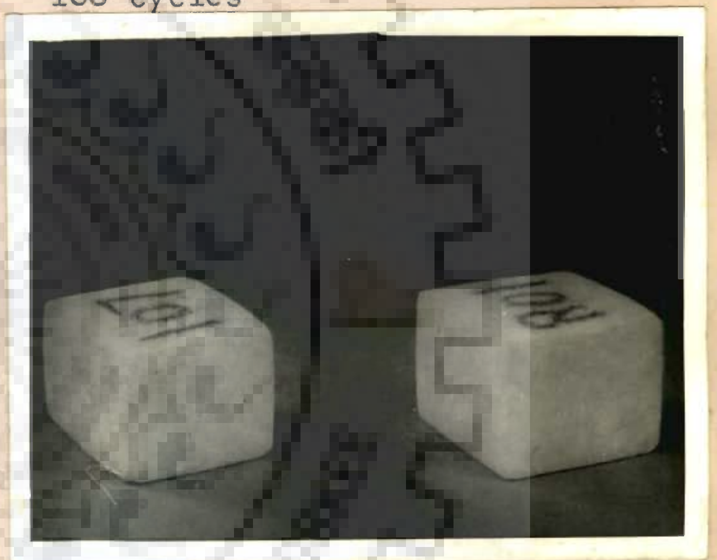


Plate 4.10: With PMMA (10%) after 100 cycles

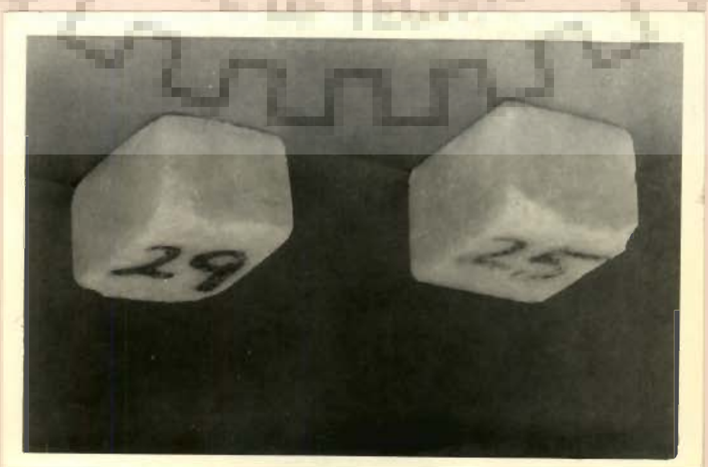


Plate 4.11: With $Ba(OH)_2$ after 87 cycles

Marble Samples Treated By Brush

Plate 4.12: With Silicone Resin after 100 cycles

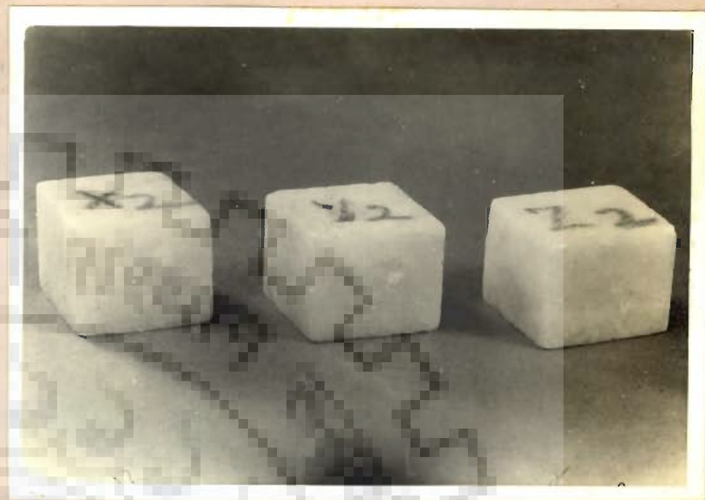


Plate 4.13: With Styrene after 100 cycles

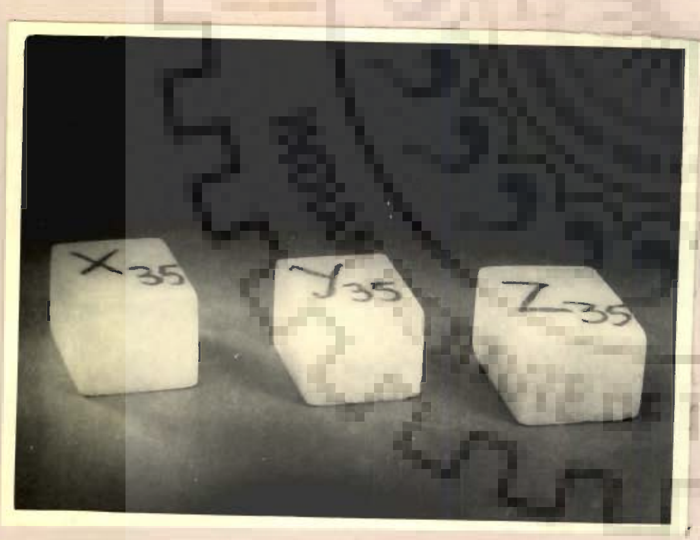


Plate 4.14: With PMMA (5%) after 100 cycles

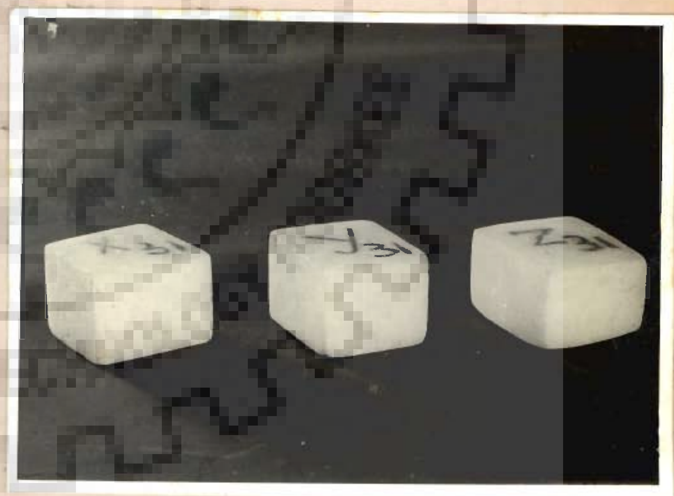


Plate 4.15: With PMMA (10%) after 100 cycles

In the case of treatment with 10 per cent PMMA the water absorption and porosity values were found to decrease from 0.083 to 0.062 and 0.24 to 0.17 per cent respectively. The values were increased to 0.115 and 0.32 per cent respectively after subjecting 100 test cycles. When the samples were treated by brush, there was a decrease of water absorption from 0.078 to 0.069 and porosity from 0.23 to 0.21 per cent. After 100 cycles of the test these were found to be increased to 0.12 and 0.37 per cent respectively. The weight loss value of the samples treated under vacuum was found to be 0.25 whereas the samples treated by brush showed 0.61 per cent weight loss after 100 cycles (Table 4.7).

By the treatment with styrene under vacuum the water absorption and porosity values decreased from 0.71 to 0.54 and 0.20 to 0.15 per cent respectively which later on increased to 0.108 and 0.30 per cent after 100 cycles of the test. When the treatment was applied by brush the values were found to decrease from 0.071 to 0.061 and 0.21 to 0.17 respectively which increased to 0.183 and 0.51 respectively after 100 cycles of the test. The weight loss of the samples treated under vacuum and brush was found to be 0.089 and 0.096 per cent respectively (Table 4.7).

The treatment with silicone resin (25 per cent) resulted into the decrease of water absorption from 0.070 to 0.051 and porosity from 0.26 to 0.14 per cent and after 100 test cycles they increased only to 0.056 and 0.16 per cent respectively. Brushing with silicone resin decreased the water absorption from 0.078 to 0.064 and porosity from 0.23

to 0.18 per cent. These samples also passed 100 cycles having 0.103, 0.29 per cent water absorption, and porosity respectively. The weight loss of both samples treated by vacuum and brushing methods was not found significant (Table 4.7).

4.3.5 Sea Water Test

Table 4.8 shows water absorption, porosity and weight loss values of untreated as well as treated marble under sea water test.

The wetting and drying cycles carried out in simulated composition of sea water show that the water absorption and porosity values of untreated marble significantly increase from 0.096 to 0.495 and 0.26 to 1.36 per cent respectively after 50 cycles of the test. The weight loss was found to be 0.27 per cent, however, the samples did not show any sign of disintegration even after 50 cycles.

The treatment with PMMA (10 per cent) and silicone resin (25 per cent) reduced the water absorption and porosity values of the stone. In the case of samples treated with PMMA these values were found to increase from 0.074 to 0.155 and from 0.21 to 0.44 per cent respectively with 0.179 per cent weight loss after subjecting them to 50 cycles of the test. The samples treated with silicone resin showed the increase of these values from 0.066 to 0.095 and 0.18 to 0.24 per cent respectively having 0.082 per cent weight loss after 50 cycles of the test.

Table 4.8

Variation in Physical Properties of Marble Samples Under Sea Water Test

Treatment	Untreated	PMMA (10%)	Silicone Resin (25%)	Untreated	PMMA (10%)	Silicone Resin (25%)	Untreated	PMMA (10%)	Silicone Resin (25%)
No. of Cycles	Water Absorption (%)			Porosity (%)			Weight loss (%)		
Initial	.096	.098	.070	.26	.27	.26	-	-	-
After coating	-	.074	.066	-	.21	.18	-	-	-
10	.187	.074	.066	.49	.21	.18	.14	.020	.040
20	.250	.110	.071	.70	.28	.20	.18	.031	.057
30	.36	.115	.085	.90	.32	.22	.21	.090	.062
40	.42	.135	.088	1.13	.37	.23	0.24	.131	.071
50	.495	.155	.095	1.36	.44	.24	0.27	.179	.082

4.3.6 Acid Test

The effect of sulphuric acid solution of different concentrations on untreated marble shows that the weight loss values varied from 4.40 to 9.81 per cent with 0.5 to 10 per cent acid solution. However, the samples treated with PMMA showed 1.85 to 6.89 per cent weight loss and for the samples treated with silicone resin it was found to be only 0.52 to 0.64 per cent with 0.5 to 10 per cent concentration of acid solution (Table 4.9).

Table 4.9

Behaviour of Marble Under Acid Test

Treatment	Untreated	PMMA (10%)	Silicone Resin (25%)
Concentration of H_2SO_4 solution (% V/V)	Weight Loss (%)		
0.5	4.40	1.85	0.52
1.0	4.71	3.04	0.56
2.0	5.30	4.35	0.59
5.0	7.05	5.50	0.61
10.0	9.81	6.89	0.64

4.4 DISCUSSION

The present study clearly indicates that the physical characteristics particularly water absorption and porosity are largely dependent on the state of the stone in terms of its degree of decay. In fresh Makrana marble samples the water absorption and porosity values have been found to be 0.08 ± 0.01 per cent and 0.23 ± 0.03 per cent respectively. Both these properties are greatly influenced by decay of the stone. Figures 4.1, 4.2 and 4.3 show progressive increase of water absorption, porosity and weight loss values respectively with the decay of the stone. Further water absorption and porosity characteristics of the stone have been found to be directly related too as shown by Fig. 4.4. It is evident from the nature of the curves that the decaying behaviour of the stone is not uniform. It has been found to be quite slow upto 20 cycles of durability test. The stone pieces did not show any significant sign of deterioration upto 30 cycles except few etch marking on the surfaces. After 30 cycles the deterioration of the stone became quite rapid as evident by the steepness of the curves. The physical data obtained also showed the similar trend. The etch markings or roughness of surface started after 30 cycles and finally (32-40 cycles) resulted into loss of the corners and development of cracks.

The durability behaviour of marble studied under test conditions 1,2 and 3, has clearly exhibited (Fig. 4.5) that variation in immersion time having same concentration of solution and drying temperature i.e. 16 hrs immersion in test condition (1) and 5 hrs in test condition (2) does not show any significant effect on decaying behaviour of the stone. The water absorption, porosity and weight loss values remain more or less same in both the test conditions. The change of drying temperature, however, has shown considerable effect on

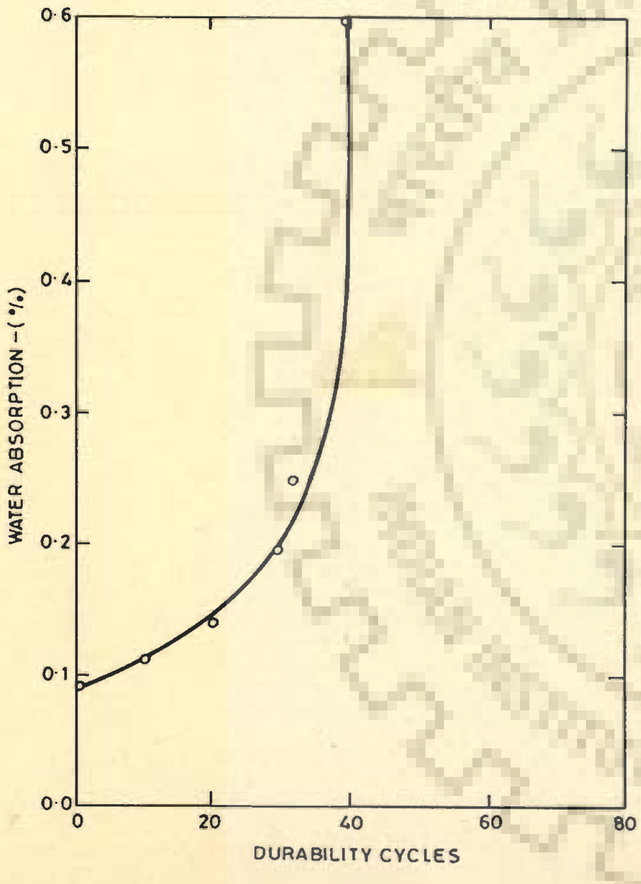


FIG. 4·1. RELATIONSHIP BETWEEN DURABILITY CYCLES & WATER ABSORPTION OF MAKRANA MARBLE

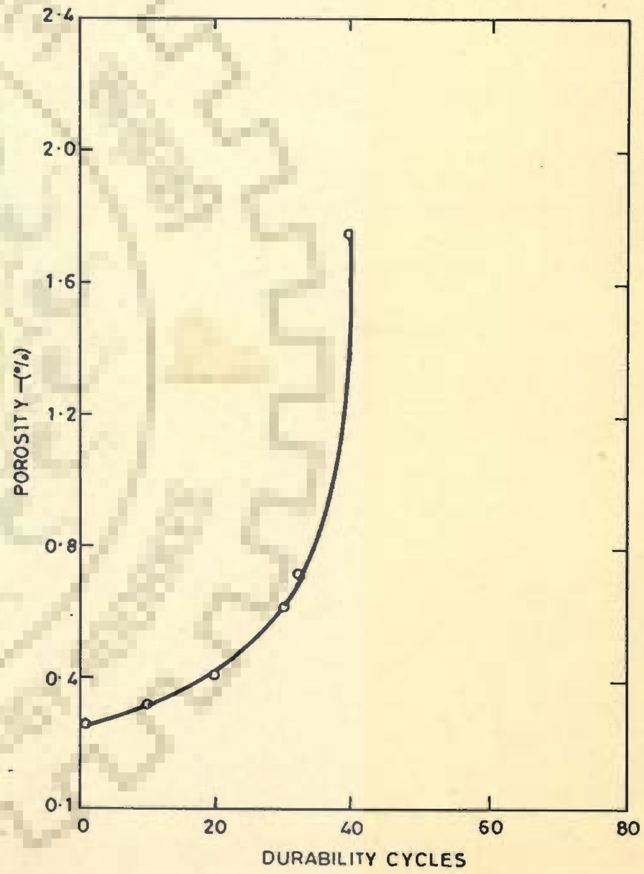


FIG. 4·2. RELATIONSHIP BETWEEN DURABILITY CYCLES & POROSITY OF MAKRANA MARBLE

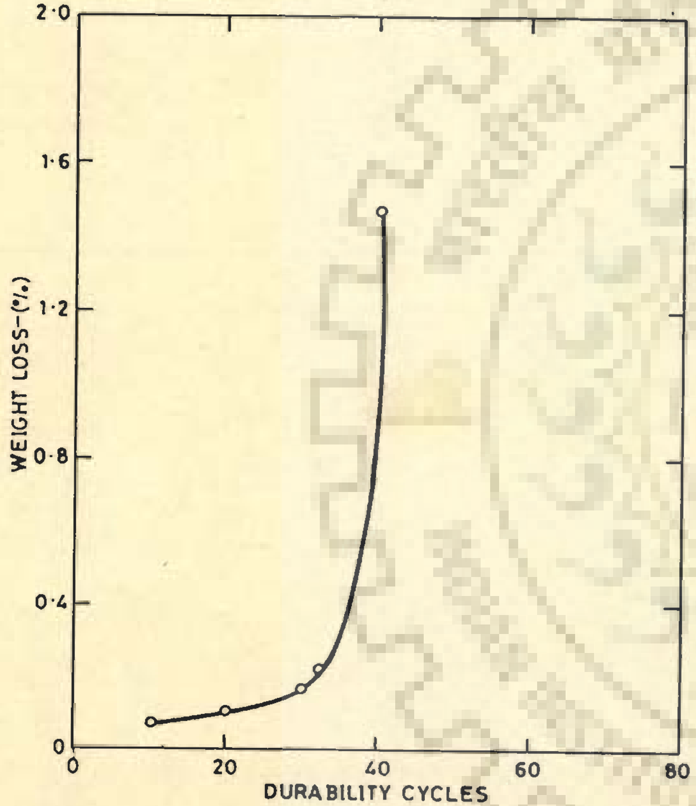


FIG.4·3. RELATIONSHIP BETWEEN DURABILITY CYCLES & WEIGHT LOSS OF MAKRANA MARBLE

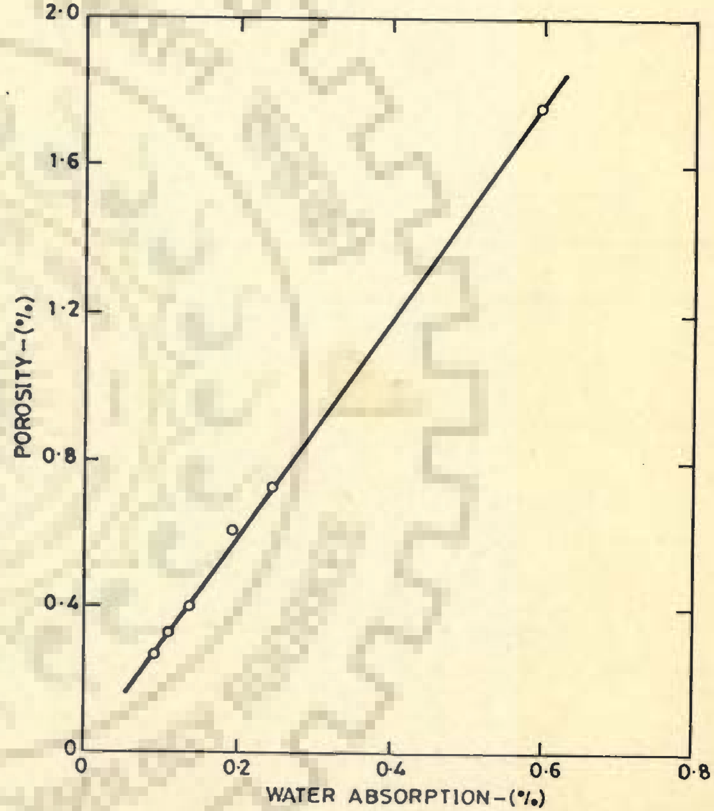


FIG.4·4. RELATIONSHIP BETWEEN POROSITY & WATER ABSORPTION OF MAKRANA MARBLE

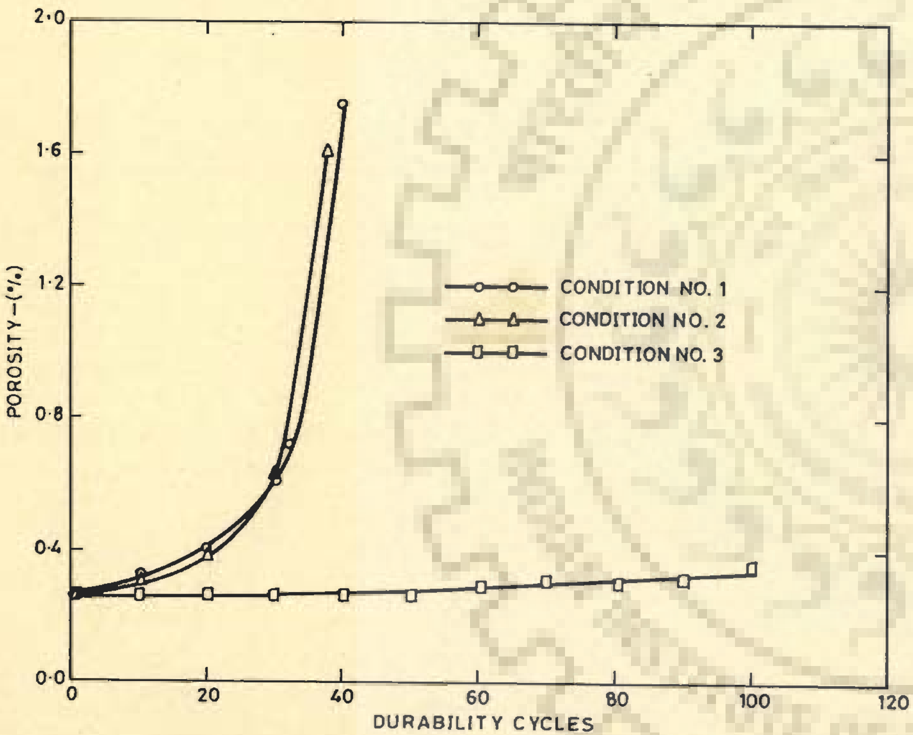


FIG.4·5. VARIATION OF POROSITY OF MARBLE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

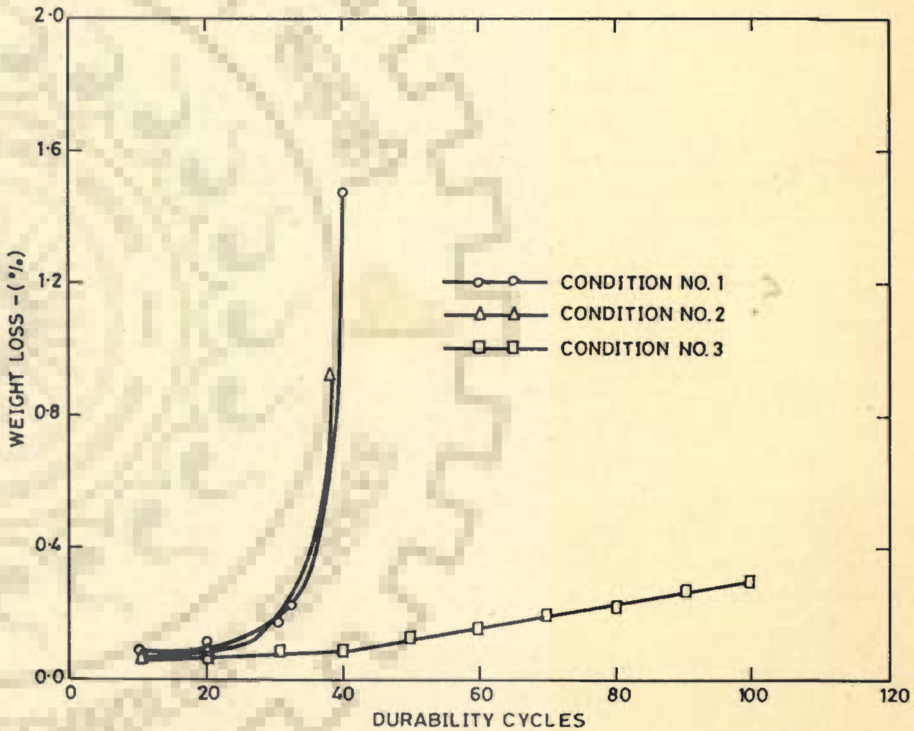


FIG.4·6. VARIATION OF WEIGHT LOSS OF MARBLE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS the durability behaviour. The samples which failed around 32-40 cycles at 105°C understood 100 cycles at 60°C. Even after 100 cycles of test at 60°C, the water absorption and porosity values were found to be much lower, 0.122and 0.35 per cent respectively in comparison to the samples which failed around 32 cycles at 105°C after attaining 0.25 and 0.72 per cent water absorption and porosity values respectively. Fig. 4.6 confirms the similar trends for weight loss values of the stone.

Thin section studies under petrographic microscope have revealed the pattern of decay of stones under durability test. It has been observed that initially the interlocking arrangement of the calcite grains become loose due to reduction in grain sizes and then the corners of calcite grains are lost. It was significant to note that initially the core or central portion of the stone show reduction in size of the calcite grains and later on a considerable reduction in grain size was observed all around. This clearly indicates that the decay of the stone starts from the central portion of the stone. Photomicrographs (Plate 4.1-4.3) show the progressive change in the characteristics of the stone.

The weathering test studies (Figs. 4.7 and 4.8) show more or less the same trends in the variations of physical characteristics of the stone. The rate of decay of the stone however, was observed to be quite slow in comparison to the durability test. Even after 100 cycles of the weathering

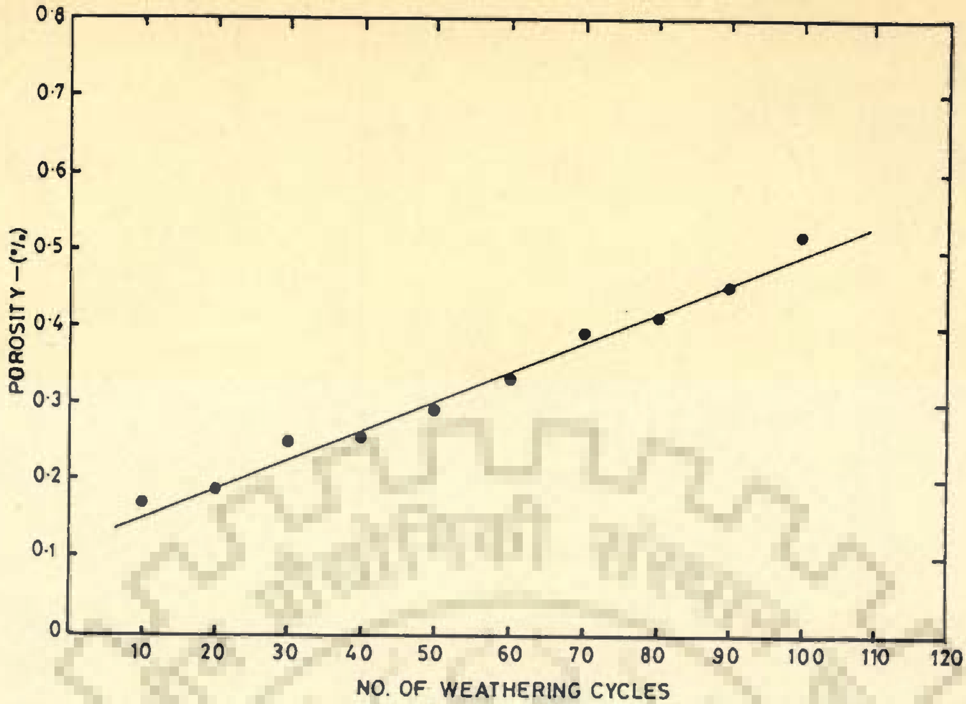


FIG.4·7. RELATIONSHIP BETWEEN WEATHERING CYCLES & POROSITY OF MAKRANA MARBLE

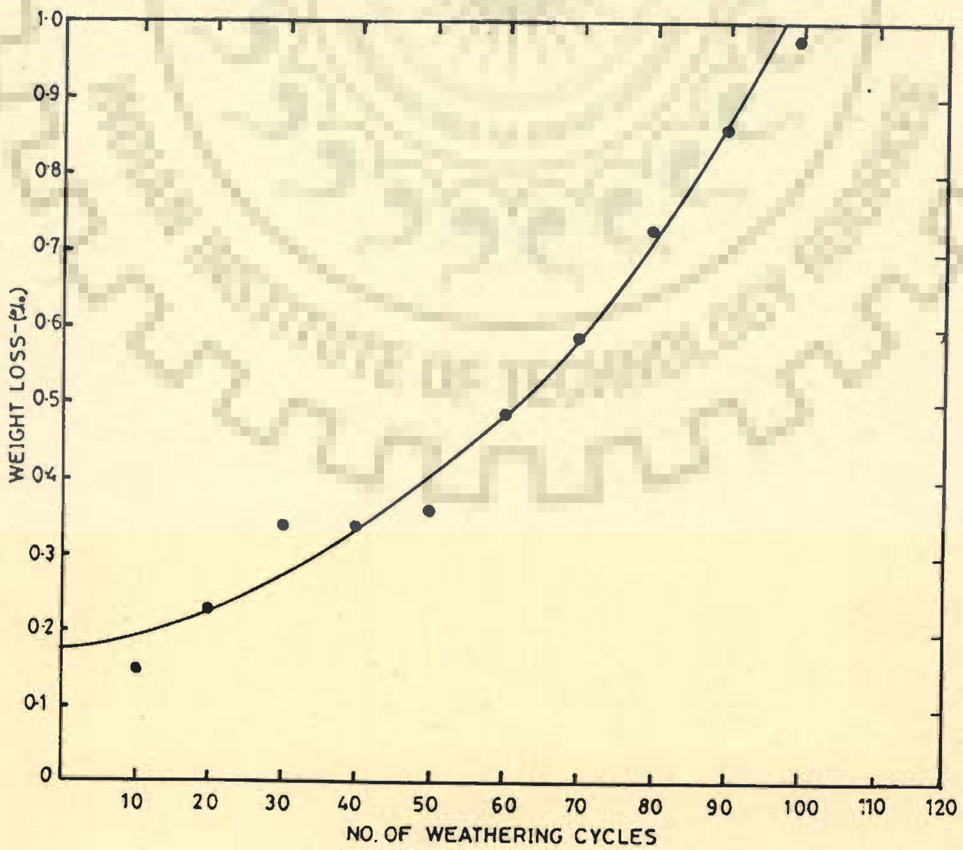


FIG.4·8. RELATIONSHIP BETWEEN WEATHERING CYCLES & WEIGHT LOSS OF MAKRANA MARBLE test the samples did not show any sign of apparent disintegration except progressive loss in weight indicating thereby some changes in physical characteristics occuring inside the stone. Thus, confirming the observations made under microscope - that the decay of the stone starts from the core of the stone.

The samples treated with different preservatives have clearly indicated that the durability of the stone in general enhances depending upon the nature of the preservative. The physical characteristics e.g. water absorption and porosity decrease considerably from the initial values. When the coating over the surface is lost the samples attain more or less original values of water absorption and porosity. The samples then behave in the same way as untreated.

Figs. 4.9 and 4.10 show the variations of porosity and weight loss values of treated marble under durability test (3). Table 4.5 exhibits the extent of reduction of the porosity values after the treatment with different preservatives. It also shows that $Ba(OH)_2$ treated samples attain the initial values of porosity after 40 cycles. After this the samples behaved as untreated (Table 4.3) and failed after 87 cycles. The possible reason for the failure of the samples could be the loss of $CaCO_3$ first forming $BaCO_3$ crystals and then removal of $BaCO_3$ leaving impressions or marking on the surface. Hence the samples behaves differently and fail completely after 87 cycles.

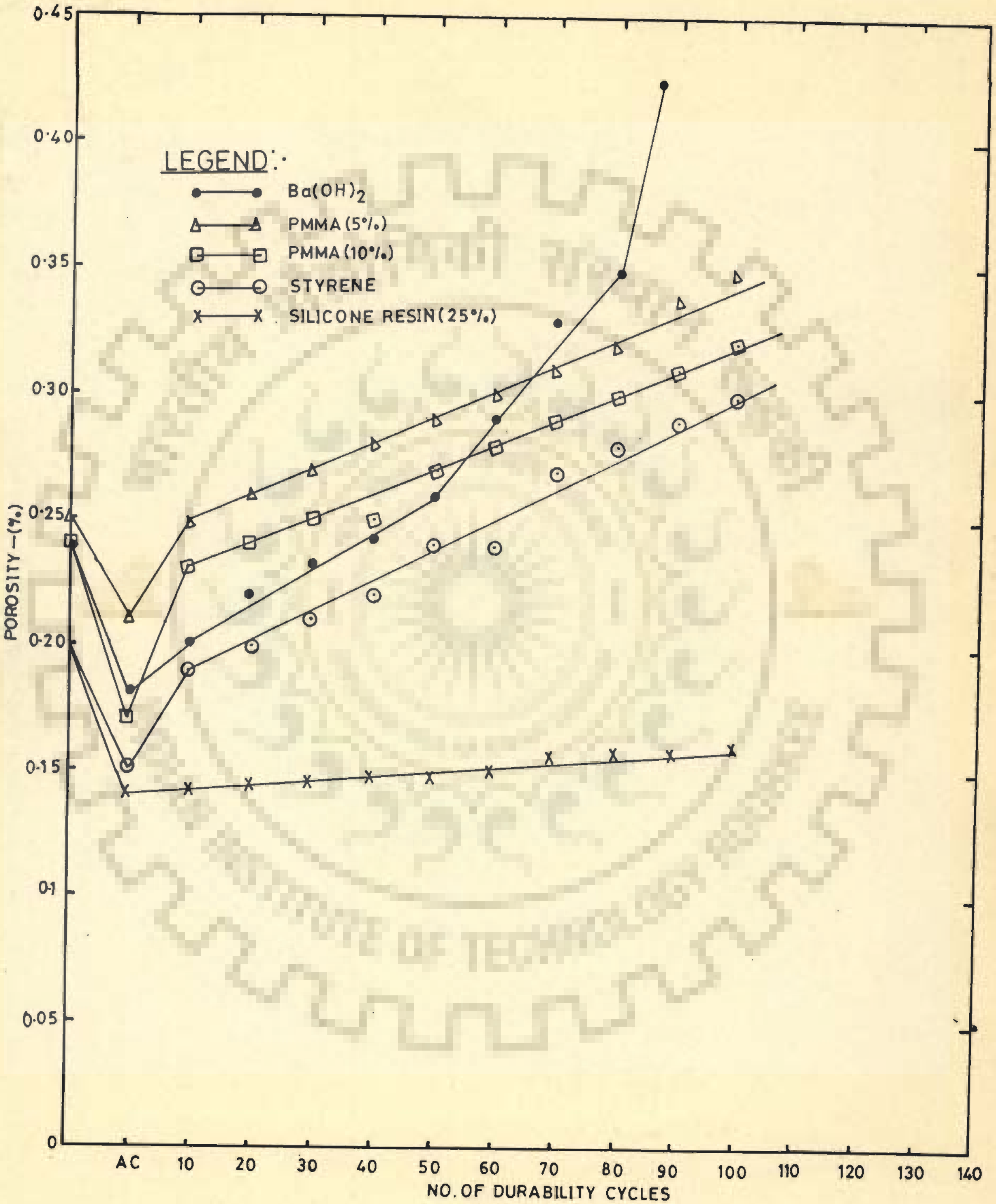


FIG. 4·9. VARIATION OF POROSITY OF TREATED MARBLE WITH DURABILITY CYCLES

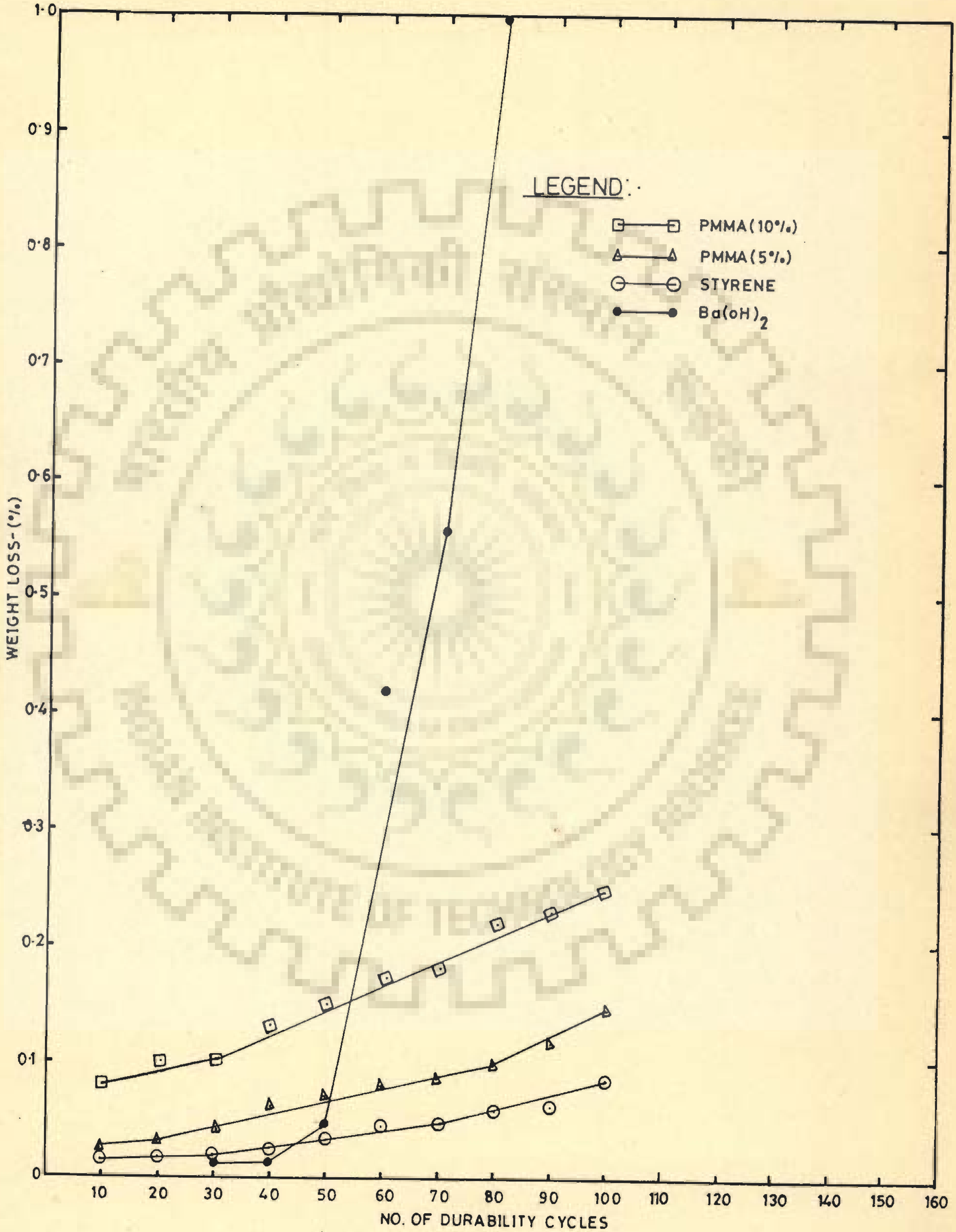


FIG.4·10. VARIATION OF WEIGHT LOSS OF TREATED MARBLE WITH DURABILITY CYCLES

The samples treated with PMMA (5 per cent) attained the original porosity after 10 cycles and then the samples behaved as untreated upto 100 cycles without any significant sign of disintegration. This clearly indicates that the effect of preservative is lost after 10 cycles. Similarly PMMA (10 per cent) is effective upto 20 cycles.

Marble samples treated with styrene showed the reduction in porosity value, the samples however, attained their initial characteristics after 20 cycles of the test. It shows that the coating of styrene lost its effect after 20 cycles and afterwards the samples behave as untreated, however, the rate of decay in the treated samples were reduced.

By the treatment with silicone resin (25 per cent) the decrease in water absorption and porosity values was found to be maximum and increase in these physical properties and weight loss after 100 test cycles was minimum. The samples could not attain initial physical characteristics up to 100 cycles indicating the effectiveness of the resin still present in the stone.

From the above discussion it is evident that the silicone resin treatment on Makrana marble may be considered to be the most effective.

Figs. 4.11 and 4.12 indicate the effect of sea-water on the durability of marble stone. The samples did not show any sign of disintegration upto 50 cycles of the test, except progressive increase in water absorption, porosity and weight

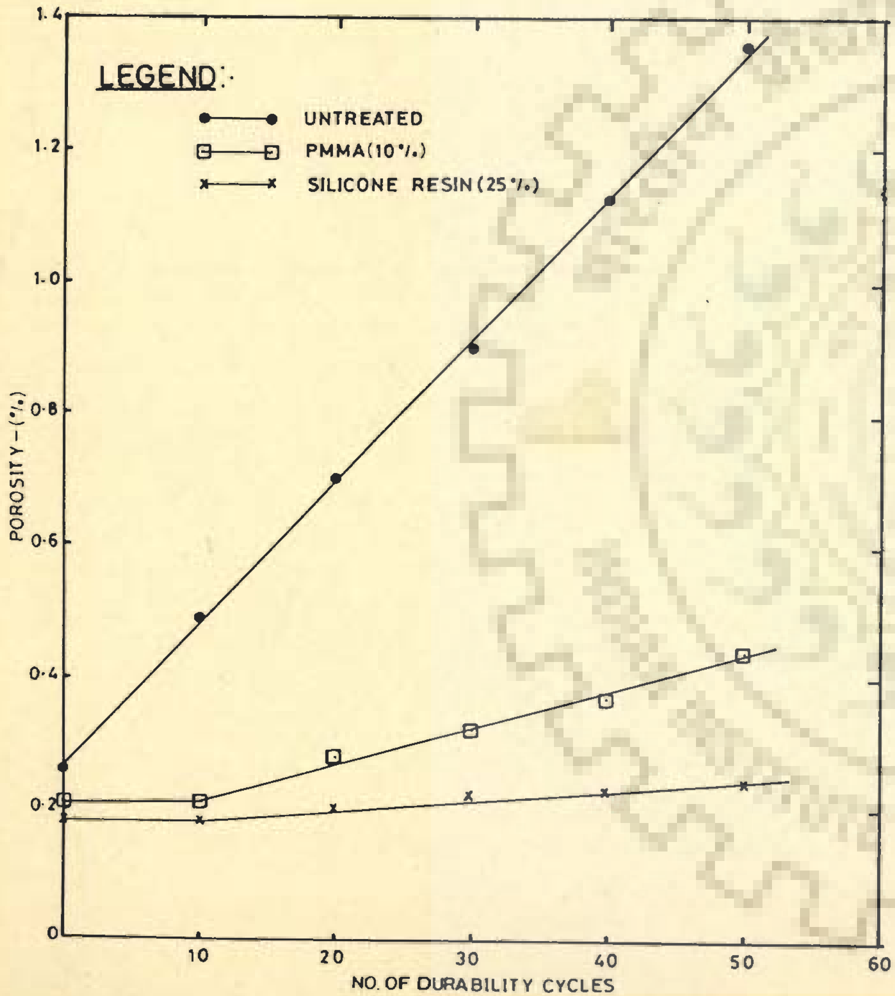


FIG. 4.11. RELATIONSHIP OF POROSITY OF MARBLE WITH DURABILITY CYCLES IN SEA WATER SOLUTION

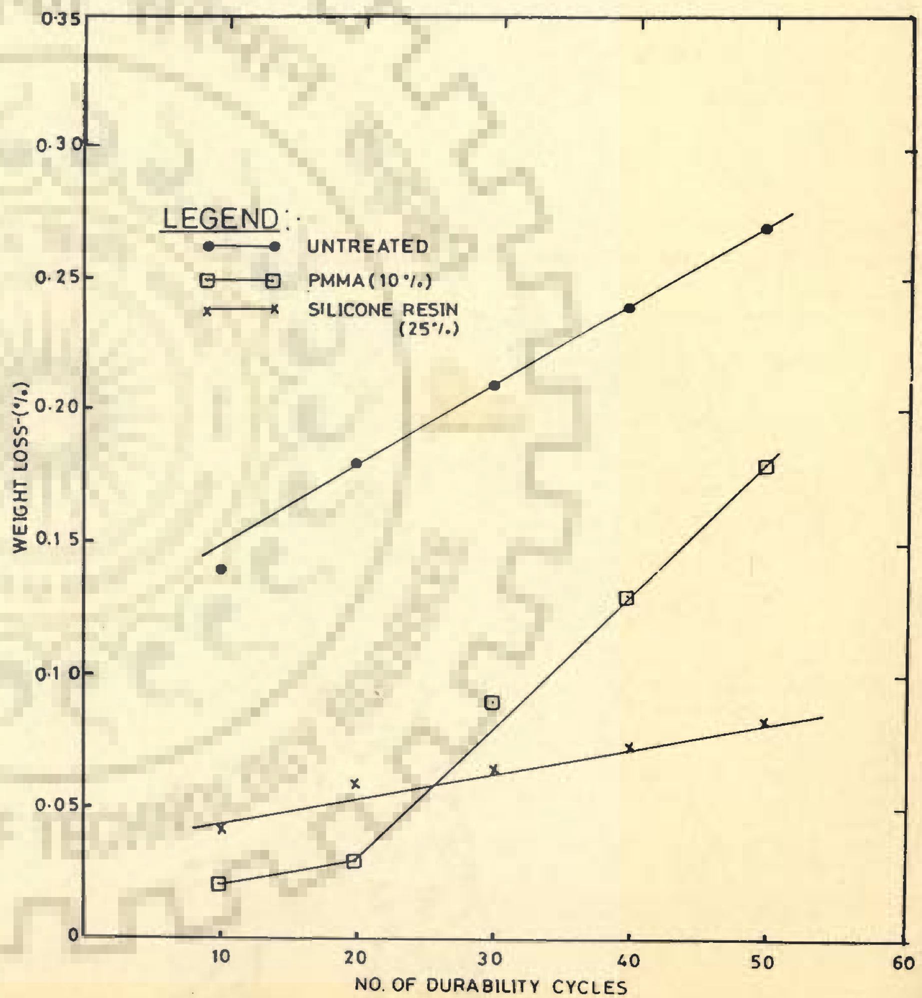


FIG. 4.12. RELATIONSHIP OF WEIGHT LOSS OF MARBLE WITH DURABILITY CYCLES IN SEA WATER SOLUTION

loss values. The samples treated with PMMA (10 percent) or silicone resin (25 per cent) showed much less increase in the physical characteristics with test cycles. Comparatively the application of silicone resin may be considered advantageous than PMMA.

Fig. 4.13 shows the effect of sulphuric acid solution on untreated and treated marble samples. It clearly indicates progressive increase in the rate of decay in the untreated as well as treated marble with the increase in concentration of acid solution. The weight loss was found more for untreated marble as the acid directly reacts with calcium carbonate of the sample resulting into the formation of calcium sulphate as per reaction given below :

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O.$$

The weight loss was reduced considerably after the treatment with PMMA and silicone resin (Table 4.9). In the case of samples treated with PMMA, calcium sulphate was deposited beneath the coating film. In 0.5 per cent acid solution the samples were not uniformly attacked while in 1.0 per cent solution $CaSO_4$ was deposited on all surfaces of the samples with the loosening of PMMA film. The thickness of $CaSO_4$ deposition increased with the concentration of acid solution and in 10 per cent solution the samples showed the pits on the surfaces due to leaching of $CaSO_4$ formed. After the test the samples showed different weight loss values before and after the washings confirming the deposition and dissolution of $CaSO_4$. In 0.5 to 5.0 per cent solution weight loss is reduced,

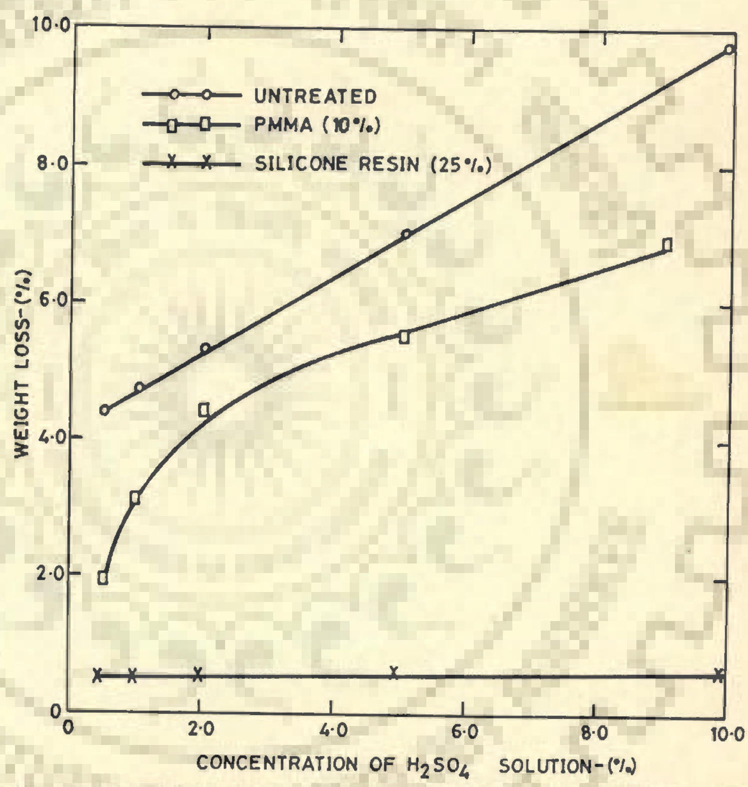


FIG. 4·13. VARIATION OF WEIGHT LOSS OF MARBLE WITH CONCENTRATION OF SULPHURIC ACID SOLUTION due to more deposition of $CaSO_4$, with the concentration of acid. In 10 per cent solution the samples showed the leaching of stone material, besides the deposition of $CaSO_4$, resulting into higher weight loss. However, after thoroughly surface washing the samples showed progressive weight loss.

In 0.5 per cent acid solution the failure of coating of silicone resin was found at the edges only, while in the case of higher concentration, the failure of coating was observed at surfaces as well as edges and corners. The effect of acid solution on coating increased with the increase in its concentration. The 10 per cent acid solution completely failed the coating and the stone itself was attacked by it, resulting into a substantial loss.

The treatments resulted into the better resistance of stone against H_2SO_4 but not absolutely. However, the treatment of stone by silicone resin may be considered more suitable.

4.5 CONCLUSION

As a result of present study several important observations have been made :

1. Physical properties like porosity and water absorption increase progressively with the increase of decay of stone. Both these properties are directly related to each other and with decaying behaviour of the stone.

2. The deterioration of the stone starts when it attains certain fixed physical properties. Among these properties water absorption and porosity values are the main factors on which the durability of the stone depends. For Makrana marble it has been found that it disintegrates only after attaining the water absorption and porosity values about 0.25 and 0.72 per cent respectively.

3. The relationship established between the physical properties and decaying behaviour of marble can be treated as standard curves for the stone. With the help of these curves one can easily predict the life of Makrana marble used in different monuments at different places and suggest the need for the preservation.

4. Silicone resin has been found to be the most suitable preservative for marble. It can easily be applied by brushing after cleaning the surface. The appearance, texture and structure of the stone remain unaffected by the application of silicone resin and also form a strong adhesion bond with the stone.

CHAPTER V

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF SANDSTONES

CHAPTER V

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF SANDSTONES

5.1 INTRODUCTION

Sandstone is a sedimentary rock formed by the deposition of sediments chiefly by water and wind. It has a bedded or stratified structure, the individual beds lying one above another. Mineralogically sandstone consists mainly of quartz cemented together by siliceous, calcareous, argillaceous or ferruginuous cementing matter. Generally the colour of the stone depends on the colour of the matrix or cementing material which may be white, grey, red, brown or yellow. In India, good sandstone deposits are known to occur in Delhi, Agra, Assam, Bengal, Gwalior, Karachi, Mirzapur, Mysore, Punjab Hills, Pachmari and Trichinopoly.

Sandstone is used for masonry work, dams, bridges, river walls, pavements etc. It is this stone which has been widely used in the construction of our historical buildings and monuments which are now in various stages of deterioration. So far no definite preservative has been found suitable for sandstone to be used in different environments. In view of this and in order to have better understanding about the factors that lead to deterioration of the stone, the present systematic study on sandstone has been taken up.

For this study sandstone samples were collected from the quarry located at Hindon, Rajasthan. In this region two very important and common varieties of sandstones are frequently found which had been and still have great demand for construction of buildings. One variety of the stone is reddish in appearance, called ''Red Sandstone'' (RS) whereas the other variety has white circular spots on the surface, called ''White Spotted Sandstone'' (WS). Most of the palaces, buildings and temples in Rajasthan, Delhi, and Northern part of India have been constructed by these two varieties of sandstone.

The present chapter describes the evaluation of physico-chemical, mineralogical, weathering and durability characteristics in terms of their inter-relationship with each other and also in predicting the durability behaviour of these stone samples under different environmental conditions. The effectiveness of different preservatives namely poly methyl methacrylate (PMMA), styrene and silicone resin have been studied under the same tests.

5.2 EXPERIMENTAL PROCEDURES

Sandstone samples both red and white spotted, were evaluated and subjected to different tests. The samples of both variety were treated with styrene, PMMA (15 percent) and Silicone resin (25 and 50 percent) and their durability behaviour was studied under the same tests. The details of the procedures followed are described in Chapter 2.

5.3 RESULTS

5.3.1 Physico-Chemical Characteristics

Physical characteristics like water absorption, porosity, specific gravity, density and compressive strength of red sandstone (RS) and white spotted sandstone (WS) samples are given in Table 5.1. It shows that the average water-absorption values for red sandstone and white spotted sandstone were found to be 3.19 and 2.78 percent whereas the porosity values were 7.75 and 6.66 percent respectively. True specific gravity was found to similar for both varieties i.e. 2.67. Apparent specific gravity was obtained to be 2.29 and 2.39 respectively. Real density was equal to 2.59 and 2.62 and bulk density 2.29 and 2.36 gm/cm^3 respectively for both varieties. The compressive strength was commonly found to be 851 and 1250 kg/cm^2 of red and white spotted sandstone respectively.

Chemical analysis data given in Table 5.1 indicate the siliceous matter in both varieties of sandstone.

5.3.2 Mineralogical Characteristics

The megascopic characters of both the sandstones indicated the rocks to be hard, compact and fine to medium grained. The characteristic difference is the presence of white circular to semi-circular patches on the surface of one sandstone designated here as white spotted sandstone. This variety of sandstone appeared to be more brittle in comparison to red sandstone. The current bedding structures present in both the varieties of stones exhibit their sedimentary origin.

Thin section studies under microscope have shown clear difference in the texture and structures of red sandstone and white spotted sandstone. In red sandstone the quartz grains commonly rounded to subrounded in shape are separated by finely crystalline siliceous and ferrugenous cementing

Table-5.1

Physico-Chemical Characteristics of Sandstones

Physical Characteristics	Average Experimental Values	
	Red Sandstone	White Spotted Sandstone
Water Absorption (% by weight)	3.19	2.78
Porosity (% by volume)	7.75	6.66
True Specific Gravity	2.67	2.67
Apparent Specific Gravity	2.29	2.36
Bulk Density (gm/cm^3)	2.29	2.36
Real Density (gm/cm^3)	2.59	2.62
Compressive Strength(Kg/cm^2)	851	1250
Hardness	4.5	5.6
Chemical Analysis		
Loss of Ignition (LOI)percent	0.71	0.99
Silica (SiO_2) ''	86.42	86.49
Aluminium Oxide (Al_2O_3) ''	4.49	2.81
Iron Oxide (Fe_2O_3) ''	6.47	5.63
Calcium Oxide (CaO) ''	0.51	2.01
Magnesium Oxide (MgO) ''	0.85	0.97

material. In case of white spotted sandstone the quartz grains in some places interlock each other particularly the portions covered by white spots and thus giving rise to quartzite character to the rock (Plates 5.1 and 5.2). The difference in the texture of rocks explains the better physico-chemical and durability characteristics of white spotted sandstone.

5.3.3 Weathering Test

The data of percentage change in porosity and weight of untreated sandstones during the weathering test is given in Table 5.2. After 100 cycles of the test the percentage change in porosity and weight of RS was found to be 0.35 and 0.0089 percent respectively while in WS the values were 4.96 and 0.13 percent respectively.

5.3.4 Durability Test

Durability studies on untreated sandstones were carried out under durability test conditions 1,2 and 3 (Table 2.2) and the data of water absorption, porosity and weight loss are given in Tables 5.3, 5.4 and 5.5.

The water absorption, porosity and weight loss values of RS after disintegration at 6 cycles under test condition (1) were found to be 4.22, 11.3 and 0.40 percent respectively, under test condition (2) these values were 3.71, 9.50 and 0.623 after 7 test cycles and under test condition (3) the values were 3.90, 10.0 and 4.24 percent respectively after disintegration at 17 cycles.

Photomicrographs showing different stages of red and white spotted sandstone before and after durability test :

Plate (5.1) Fresh red sandstone showing mainly rounded to subrounded quartz grains embedded in ferrugenous and siliceous ground mass (X100)

Plate (5.2) Fresh white spotted sandstone showing pseudo-quartzitic to quartizitic texture. The quartz grains are generally subrounded to irregular in shape with iron minerals as independent grains (X100)

Plate (5.3) Red sandstone, after durability test, slight to moderately altered rock showing changes in shape and sizes of quartz grains with more ferrugenous matter (X100)

Plate (5.4) White spotted sandstone, after durability test, slight to moderately altered rock lacking in quartzitic texture. The quartz grains are generally rounded to subrounded in shape separated by ferrugenous cementing material. Iron minerals are commonly present (X100)

RED SANDSTONE

WHITE SPOTTED SANDSTONE

Plate 5.1: Before Durability Test x100

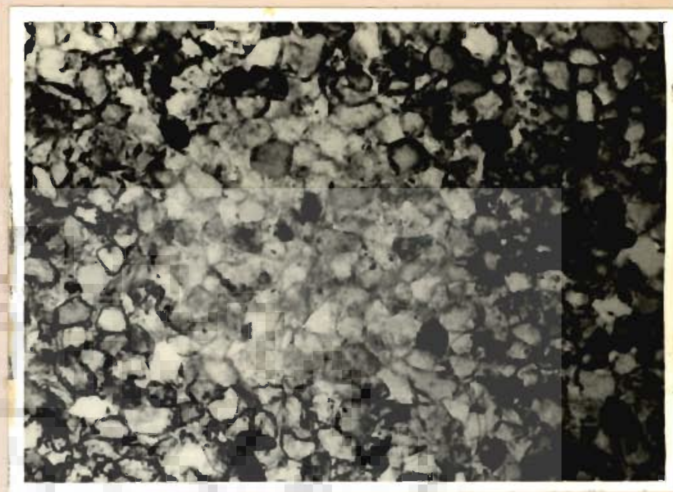


Plate 5.2: Before Durability Test x100

Plate 5.3: After Durability Test x100

Plate 5.4: After Durability Test x100

Table 5.2

Variation in Physical Characteristics of Sandstones Under Weathering Test

No. of Cycles	% Change in Porosity		% Change in Weight loss	
	Red Sandstone (RS)	White spotted Sandstone (WS)	Red Sandstone (RS)	White spotted Sandstone (WS)
10	-0.33	-0.57	+0.0085	+0.022
20	-3.6	-1.75	+0.060	+0.040
30	-4.7	-2.25	+0.092	+0.064
40	-6.7	-2.60	+0.15	+0.086
50	-7.6	-2.75	+0.24	+0.106
60	-5.0	-2.00	+0.14	+0.027
70	-2.5	+3.33	+0.083	-0.013
80	-0.42	+4.23	+0.058	-0.06
90	–	+4.65	–	-0.10
100	+0.35	+4.96	-0.0089	-0.13

Table 5.3

Variation in Water Absorption Values of Sandstones Under Different Durability Test Conditions

Sample	Red Sandstone (RS)			White Spotted Sandstone (WS)			
Test Condition	(1)	(2)	(3)		(1)	(2)	(3)
No. of Cycle	Water Absorption (%)				Water Absorption (%)		
Inital	3.20	3.21	3.27	Initi-al	2.78	2.76	2.68
5	3.35	3.30	3.43	5	2.80	2.96	2.75
6	4.22*	-	-	10	2.95	3.00	2.93
7	-	3.71*	-	14	3.10*	-	-
8	4.31	-	-	15	3.22	3.09*	3.04
9	-	4.68**	-	16	3.60**	-	-
10	4.51**		3.62	17	-	3.55**	3.24*
17	-		3.90*	20	-	-	3.33
20	-		4.45**	23	-	-	3.38**

*Appearance of crack

**Samples badly cracked

Table 5.4

Variation in Porosity Values of Sandstones Under Different Durability Test Conditions

Sample	Red Sandstone (RS)				White Spotted Sandstone(WS)		
Test Condition	(1)	(2)	(3)		(1)	(2)	(3)
No. of cycle	Porosity (%)			No.of cycle	Porosity (%)		
Initial	8.50	8.27	8.66	Initial	6.68	6.74	6.54
5	8.71	8.50	8.80	5	6.70	6.84	6.67
6	11.3*	-	-	10	6.89	6.98	6.92
7	-	9.50*	-	14	7.31*	-	-
8	11.5	-	-	15	7.85	7.20*	7.04
9	-	12.0**	-	16	8.50**	-	-
10	11.7**	-	9.28	17	-	8.27**	7.25*
17.	-	-	10.0*	20	-	-	7.49
20	-	-	11.4**	23	-	-	8.16**

*Appearance of crack

**Samples badly cracked

Table 5.5

Variation in Weight loss values of Sandstones
Under Different Durability Test Conditions

Sample	Red Sandstone (RS)				White Spotted Sandstone (WS)		
Test Condition	(1)	(2)	(3)		(1)	(2)	(3)
No. of cycle	Weight loss (%)			No. of cycle	Weight loss (%)		
5	0.235	0.274	0.829	5	0.205	0.521	0.572
6	0.400*	-	-	10	0.746	1.20	0.746
7	-	0.623*	-	14	1.83*	-	-
8	0.574	-	-	15	2.10	2.80*	2.30
9	-	2.08**	-	16	2.50**	-	-
10	1.75**	-	2.40	17	-	3.32**	2.96*
17	-	-	4.24*	20	-	-	3.47
20	-	-	7.81**	23	-	-	5.56**

*Appearance of crack

**Samples badly cracked

Likewise, samples or WS were found to have these values as 3.10, 7.31 and 1.83 percent after disintegration at 14 cycles under test condition (1), 3.09, 7.20 and 2.80 percent after 17 cycles under test condition (2) and under test condition (3) these values were 3.24, 7.25 and 2.96 percent respectively after disintegration at 23 cycles of the test. These values of both RS and WS samples were found to be slightly increased with the decaying test cycles. The failure of both samples can be clearly seen from the photographs (Plates 5.5-5.10).

The water absorption, porosity and weight loss values of both varieties of sandstone treated with different preservatives during the durability test (3) are given in tables 5.6, 5.7 and 5.8.

The sandstone samples treated with PMMA (15 percent) were badly disintegrated after 90 cycles of the test, however, the coating started to separate from the stone surfaces after 20-30 cycles in the case of RS and 50 cycles in WS samples. The coating carried out by brushing method failed after 7-10 cycles in RS and after 10-11 cycles in WS sandstone samples. The samples of both varieties disintegrated at about 20 cycles of the test when treated by brush (Plates 5.21, 5.22) and after 90 cycles when treated under vacuum technique (Plates 5.11-5.16).

After the vacuum treatment of PMMA (15 percent) the water absorption and porosity values of RS were decreased from 3.27 to 0.27 and from 7.15 to 0.54 percent respectively. After 90 cycles of the test these values were increased to 3.92 and

Table 5.6

Variation in Water Absorption Values of Treated Sandstones Under Durability Test (3)

Treatment	Silicone Resin (50%)		Styrene		PMMA (15%)	
Sample	RS	WS	RS	WS	RS	WS
No. of cycle	Water Absorption (%)					
Initial	3.31	2.71	2.79	2.89	3.27	2.66
After coating	0.130	0.170	0.10	0.066	0.27	0.58
10	0.131	0.171	0.18	0.123	0.35	0.605
20	0.135	0.172	0.19	0.132	0.43	0.724
30	0.138	0.174	0.20	0.169	0.54	0.863
40	0.137	0.175	0.20	0.176	0.83	0.885
50	0.139	0.177	0.21	0.184	1.12	1.09
60	0.140	0.181	0.22	0.192	1.52	1.43
70	0.144	0.180	0.23	0.184	2.08	1.79
80	0.142	0.181	0.24	0.192	2.86	2.63
90	0.145	0.182	0.22	0.190	3.92*	3.18*
100	0.147	0.185	0.24	0.193	-	-

*Samples badly disintegrated.

Table 5.7

Variation in Porosity Values of Treated Sandstones Under Durability Test Condition (3)

Treatment	Silicone Resin (50%)		Styrene		PMMA (15%)	
Sample	RS	WS	RS	WS	RS	WS
No. of Cycle	Porosity (%)					
Initial	7.06	6.27	6.32	6.83	7.15	6.01
After Coating	0.300	0.390	0.26	0.16	0.54	1.39
10	0.306	0.390	0.43	0.30	0.77	1.43
20	0.310	0.400	0.43	0.32	0.95	1.70
30	0.315	0.402	0.44	0.42	1.18	1.88
40	0.317	0.406	0.43	0.43	1.78	2.09
50	0.324	0.410	0.47	0.45	2.55	2.58
60	0.330	0.412	0.48	0.47	3.46	3.39
70	0.335	0.417	0.52	0.45	4.53	4.24
80	0.340	0.420	0.54	0.47	5.49	5.63
90	0.342	0.425	0.52	0.46	8.00*	7.35*
100	0.344	0.427	0.54	0.49	-	-

*Samples badly disintegrated

Table 5.8

Variation in Weight loss Values of Treated Sandstone Under Durability Test (3)

Treatment	Silicone Resin (50%)		Styrene		PMMA (15%)	
Sample	RS	WS	RS	WS	RS	WS
No. of cycle	Weight loss (%)					
10	0.26	0.26	0.098	0.13	0.17	0.155
20	0.27	0.33	0.10	0.13	0.20	0.235
30	0.25	0.26	0.10	0.14	0.30	0.40
40	0.24	0.35	0.11	0.14	0.40	0.55
50	0.24	0.39	0.12	0.15	0.70	0.730
60	0.25	0.38	0.12	0.15	1.10	1.0
70	0.27	0.39	0.13	0.16	1.50	1.80
80	0.28	0.37	0.14	0.16	2.13	2.38
90	0.30	0.44	0.14	0.17	3.60*	3.25*
100	0.32	0.45	0.15	0.18	-	-

*Samples badly disintegrated

RED SANDSTONE

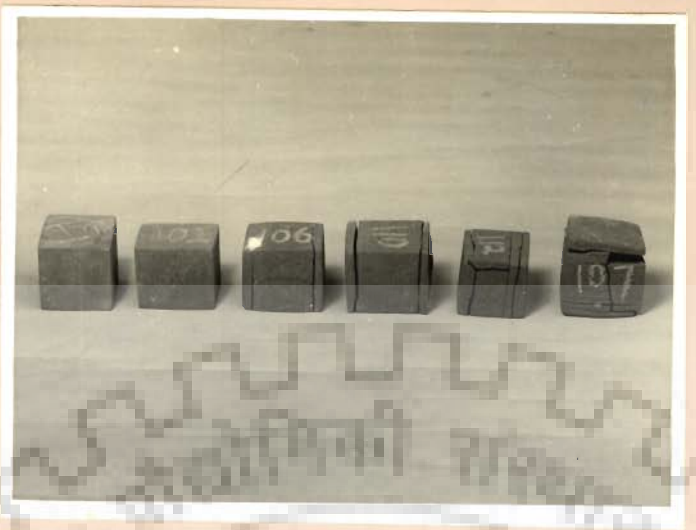


Plate 5.5 : Durability behaviour under test condition (1)

Plate 5.6 : Durability behaviour under test condition (2)

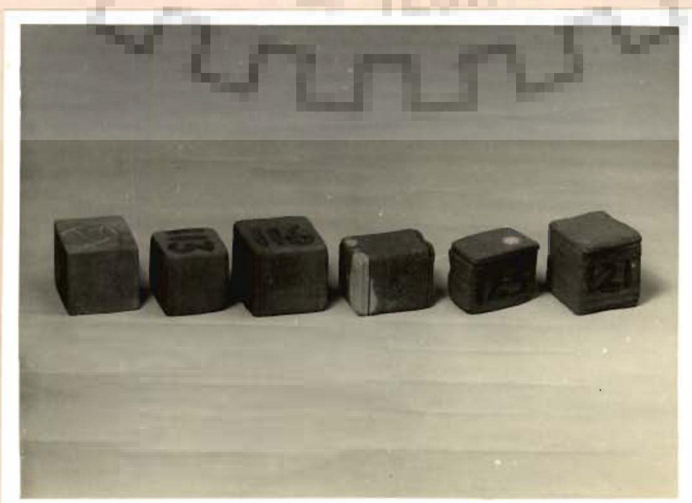


Plate 5.7 : Durability behaviour under test condition (3)

WHITE SPOTTED SANDSTONE

Plate 5.8 : Durability behaviour under test condition (1)

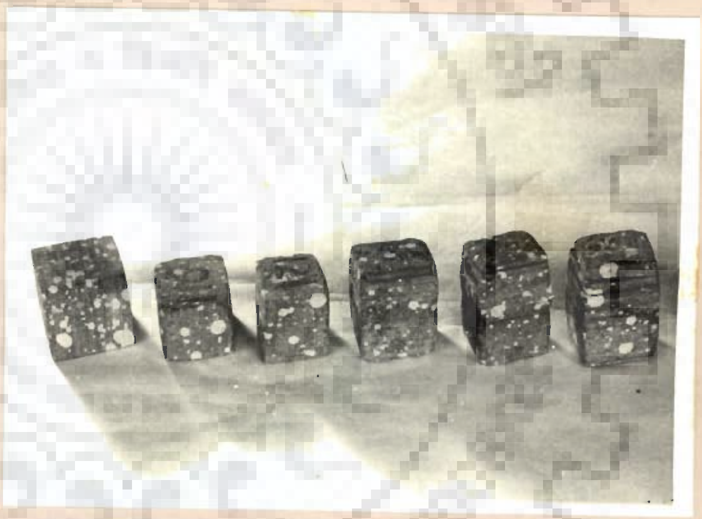


Plate 5.9 : Durability behaviour under test condition (2)

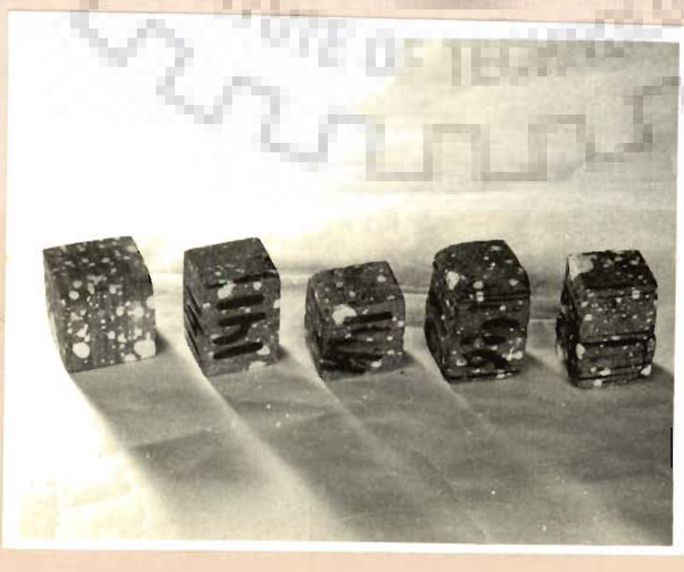


Plate 5.10: Durability behaviour under test condition (3)

Sandstone Samples Treated Under Vacuum

RED SANDSTONE

WHITE SPOTTED SANDSTONE

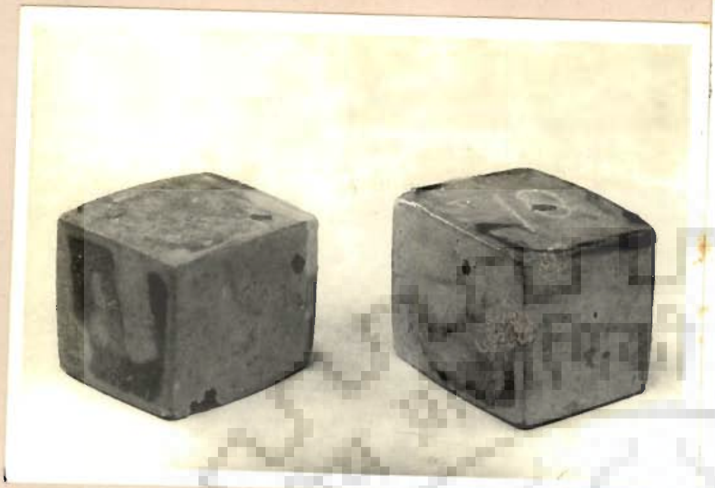


Plate 5.11: Failure of PMMA coating after 30 cycles

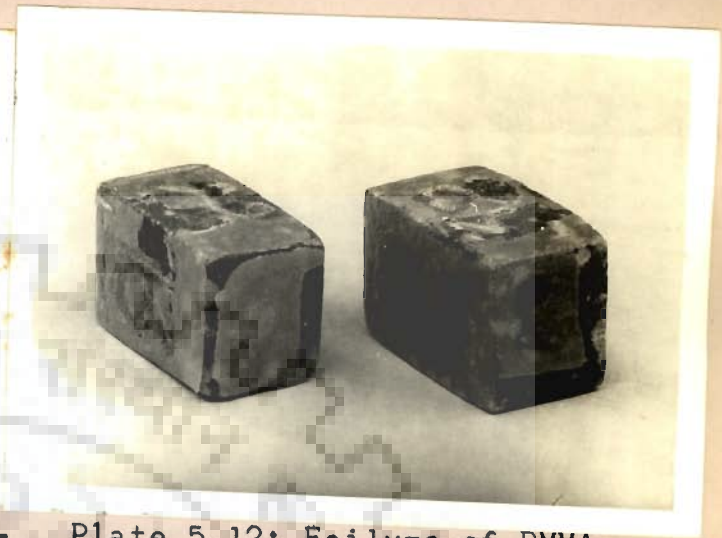


Plate 5.12: Failure of PMMA coating after 50 cycles

Plate 5.13: Development of cracks after 70 cycles

Plate 5.14: Development of cracks after 70 cycles

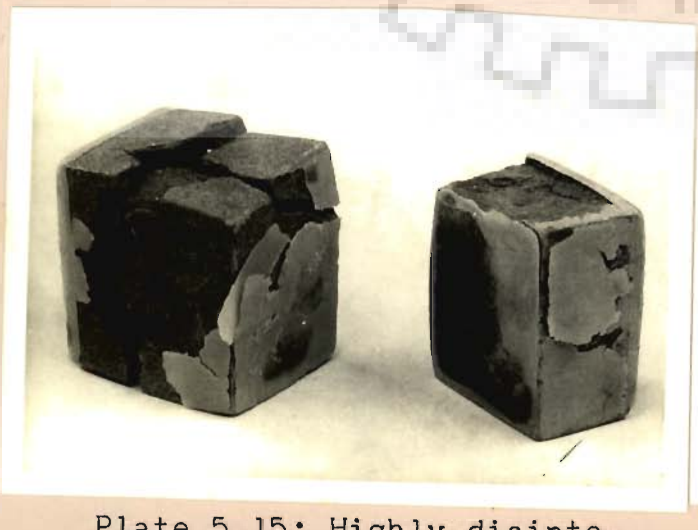


Plate 5.15: Highly disintegrated after 90 cycles

Plate 5.16: Highly disintegrated after 90 cycles

8.00 percent respectively. The samples coated by brush showed the decrease of water absorption value from 3.29 to 1.77 per cent and porosity from 8.47 to 4.57 per cent which were found to increase to 3.31 and 7.69 per cent respectively after 20 cycles. The samples treated by vacuum showed the weight loss value 3.60 per cent after 90 cycles while the samples treated by brush have 9.74 per cent weight loss after 20 cycles of the test (Table 5.9).

The treatment of WS samples resulted into the decrease of water absorption from 2.66 to 0.58 and porosity from 6.01 to 1.39 per cent. After 90 cycles of the test these values were increased to 3.18 and 7.35 per cent respectively. The brushing method decreased these values from 2.85 to 1.39 and 7.61 to 3.72 per cent respectively, which were found to increase 3.60 and 8.74 per cent respectively only after 20 cycles. The weight loss of samples treated by vacuum method was found to be 3.25 per cent after 100 cycles of the test, whereas the samples treated by brushing method showed 7.07 per cent weight loss only after 20 cycles of the test (Table 5.10).

The sandstone samples of both varieties treated with styrene and silicone resin under vacuum technique passed 100 cycles of the test without showing any sign of coating failure or sample disintegration (Plates 5.17-5.20).

By the treatment with styrene under vacuum the water absorption and porosity values of RS decreased from 2.79 to 0.10 and 6.32 to 0.26 per cent respectively which later on increased

Sandstone Samples Treated Under Vacuum

RED SANDSTONE	WHITE SPOTTED SANDSTONE

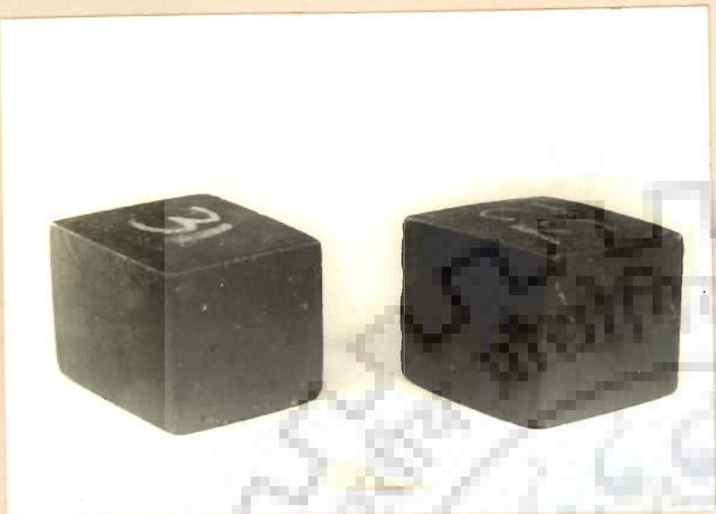


Plate 5.17: Silicone Resin treated samples after 100 cycles

Plate 5.18: Silicone Resin treated samples after 100 cycles

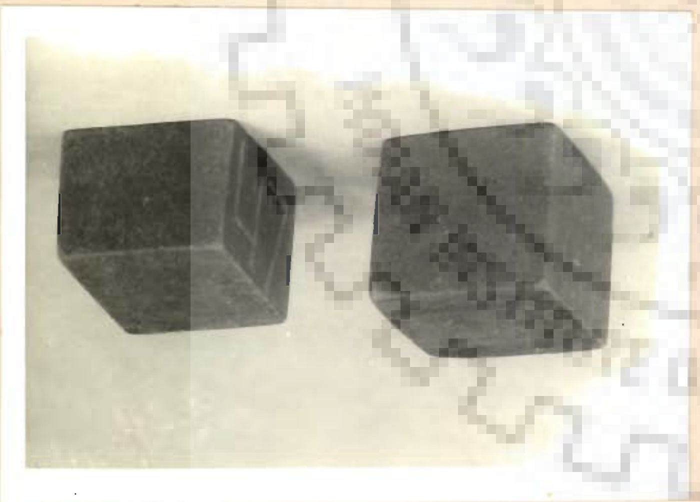


Plate 5.19: Styrene treated samples after 100 cycles

Plate 5.20: Styrene treated samples after 100 cycles

to 0.24 and 0.54 per cent respectively after 100 cycles. When the treatment was applied by brush the coating failed after 12 cycles and samples after 20 cycles. The values on coating were found to decrease from 3.33 to 0.41 and 7.55 to 1.0 per cent respectively which increased to 3.19 and 6.93 per cent respectively after 20 cycles. The weight loss of the samples treated under vacuum was 0.15 per cent after 100 cycles and 5.57 per cent of samples treated by brush after 20 cycles of the test (Table 5.9).

The treatment of WS samples resulted into the decrease of water absorption and porosity values from 2.89 to 0.066 and 6.83 to 0.16 percent respectively. After 100 cycles of the test these values were found to be increased 0.193 and 0.49 percent respectively. The weight loss of the samples was 0.18 percent after 100 cycles of the test. The treatment by brush resulted into the decrease of water absorption and porosity values from 2.95 to 0.31 and 7.21 to 0.79 per cent respectively. These values were increased to 3.10 and 6.45 percent respectively after 20 cycles. The samples failed after 20 cycles having 6.70 percent weight loss (Table 5.10). The treatment with silicone resin (50 percent) resulted into the decrease of water absorption from 3.31 to 0.13 and porosity from 7.06 to 0.30 percent respectively of RS samples. After 100 cycles of the test the values were found to be increased only 0.147 and 0.344 percent respectively. The weight loss was 0.32 percent. Brushing resulted into the failure of coating after 30 cycles and samples were badly disintegrated after 40 cycles of the test (Plate 5.23). The water absorption and porosity values decreased by

Table-5.9

Durability Behaviour of Red Sandstone

Untreated/ Treated	Test condition	Initial Water Absorption (%)	Initial Porosity (%)	After Coating Water Absorption (%)	After Coating Porosity (%)	Disintegration Cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)	Rate of Decay (Wt.loss/ cycle)
Untreated	(1)	3.20	8.50	-	-	6-10	4.22	11.3	0.400	0.066
	(2)	3.21	8.27	-	-	7-10	3.71	9.50	0.603	0.086
	(3)	3.27	8.66	-	-	17-20	3.90	10.0	4.24	0.25
Treated with PMMA (15%)	(3)									
Under Vacuum		3.27	7.15	0.27	0.54	90	3.92	8.00	3.60	0.406
By Brushing		3.29	8.47	1.77	4.57	20	3.31	7.69	9.74	0.486
Styrene	(3)									
Under Vacuum		2.79	6.32	0.10	0.26	100*	0.24	0.54	0.15	0.0015
By Brushing		3.33	7.55	0.41	1.0	20	3.19	6.93	5.57	0.279
Silicone Resin (50%)	(3)									
Under Vacuum		3.31	7.06	0.13	0.30	100*	0.147	0.344	0.32	0.0032
By Brushing		3.29	7.67	1.2	2.66	40	4.22	7.25	11.8	0.295

*Samples not disintegrated

Table-5.10

Durability Behaviour of White Spotted Sandstone

Untreated/ Treated	Test condition	Initial		After Coating		Disin- tegra- tion Cycle	Final		Weight loss	Rate of Decay (Wt.loss/ cycle)
		Water Absorp- tion (%)	Porosity (%)	Water Absorp- tion (%)	Porosity (%)		Water Absor- ption (%)	Porosity (%)	(%)	
Untreated	(1)	2.78	6.68	-	-	14-16	3.10	7.31	1.83	.130
	(2)	2.76	6.74	-	-	15-17	3.09	7.20	2.80	.180
	(3)	2.68	6.54	-	-	17-23	3.24	7.25	2.96	.180
Treated with PMMA (15%)	(3)									
Under Vacuum		2.66	6.01	0.58	1.39	90	3.18	7.35	3.25	.361
By Brushing		2.85	7.61	1.39	3.72	20	3.60	8.74	7.07	.354
Styrene	(3)									
Under Vacuum		2.89	6.83	0.066	0.16	100*	0.193	0.49	0.18	.0018
By Brushing		2.95	7.21	0.31	0.79	20	3.10	6.45	6.70	.335
Silicone Resin (50%)	(3)									
Under Vacuum		2.71	6.27	0.17	0.39	100*	0.185	0.427	0.45	.0045
By Brushing		2.81	6.48	0.99	2.04	40	3.23	6.25	9.24	23.1

*Samples not disintegrated

Sandstone Samples Treated by Brush

RED SAND STONE

WHITE SPOTTED SANDSTONE

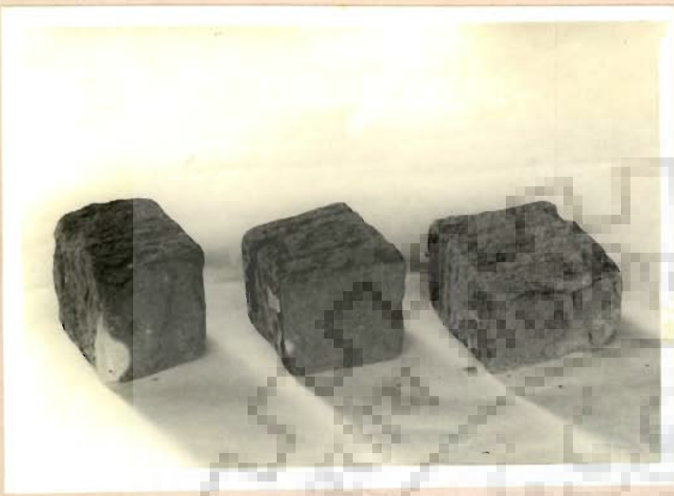


Plate 5.21: Failure of PMMA treated samples after 20 cycles

Plate 5.22: Failure of PMMA treated samples after 20 cycles

Plate 5.23: Failure of Silicone Resin treated samples after 40 cycles

Plate 5.24: Failure of Silicone Resin treated samples after 40 cycles

brushing from 3.29 to 1.2 and 7.67 to 2.66 percent respectively. After 40 cycles of the test the samples have 4.22, 7.25 and 11.8 percent water absorption porosity and weight loss respectively (Table 5.9).

In the case of WS samples, silicone resin resulted into the decrease of these values from 2.71 to 0.17 and 6.27 to 0.39 percent. After 100 cycles of the test these values were found to be 0.185 and 0.427 percent respectively along with 0.45 percent weight loss. However, silicone resin coated by brush decreased the water absorption and porosity values from 2.81 to 0.99 and 6.48 to 2.04 percent respectively. The samples failed after 40 cycles (Plate 5.24) having 3.23, 6.25 and 9.24 percent water absorption, porosity and weight loss respectively (Table 5.10).

5.3.6 Sea Water Test

The wetting and drying cycles carried out in sea water composition show that the water absorption and porosity values of untreated red sandstone increases from 3.25 to 3.53 and 7.50 to 8.28 percent respectively. The weight loss was found to be 3.67 percent, however, the samples did not show any sign of disintegration even after 50 cycles. In the case of samples treated with silicone resin these values of water absorption, porosity and weight loss were decreased to 0.401, 0.940 and 0.057 percent respectively, whereas the values were 1.10, 2.25 percent treated with PMMA, after 50 cycles of the test (Tables 5.11, 5.12, 5.13). The samples treated with PMMA did not show

Table 5.11

Variation in Water Absorption Values of Sandstones Under Sea Water Test

Treatment	Untreated		PMMA(15%)		Silicone Resin(25%)	
Sample	RS	WS	RS	WS	RS	WS
No. of cycle	Water Absorption (%)					
Initial	3.25	2.70	3.73	3.11	3.60	2.87
After coating	-	-	0.350	1.14	0.341	0.15
10	3.30	2.74	0.365	2.10	0.358	0.182
20	3.38	2.88	0.488	2.38	0.364	0.218
30	3.43	2.98	0.704	2.54	0.388	0.322
40	3.48	3.06	0.874	2.60	0.399	0.441
50	3.53	3.12	1.10	2.70	0.401	0.651

Table 5.12

Variation in Porosity Values of Sandstones Under Sea Water Test

Treatment	Untreated		PMMA(15%)		Silicone Resin (25%)	
Sample	RS	WS	RS	WS	RS	WS
No. of cycle	Porosity (%)					
Initial	7.50	6.47	8.41	7.21	7.99	6.55
After coating	-	-	0.801	2.67	0.761	0.33
10	7.54	6.51	0.960	4.93	0.800	0.439
20	7.82	6.65	1.22	5.68	0.810	0.506
30	7.90	6.80	1.59	5.90	0.865	0.765
40	8.15	7.40	1.79	6.00	0.900	1.04
50	8.28	7.80	2.25	6.20	0.940	1.51

Table 5.13

Variation in Weight loss Values of Sandstones Under Sea Water Test

Treatment	Untreated		Silicone Resin (25%)		PMMA (15%)	
Sample	RS	WS	RS	WS	RS	WS
No. of cycle		Weight loss (%)				
10	3.46	0.10	0.017	0.089	Insignificant	
20	3.49	0.12	0.028	0.095	''	
30	3.55	0.15	0.039	0.105	''	
40	3.59	0.19	0.051	0.117	''	
50	3.67	0.24	0.057	0.125	''	

Table 5.14

Behaviour of Sandstones Under Acid Test

Concentration of H_2SO_4 solution (%) (V/V)	Untreated		PMMA (15%)		Silicone Resin (25%)	
	RS	WS	RS	WS	RS	WS
0.5	0.119	0.023	0.085	0.087	0.062	0.086
1.0	0.181	0.031	0.086	0.092	0.065	0.086
2.0	0.195	0.043	0.094	0.097	0.064	0.086
5.0	0.259	0.067	0.120	0.112	0.069	0.087
10.0	0.301	0.096	0.159	0.151	0.065	0.086

any significant weight loss. Similar trends were found for white spotted sandstone.

5.3.7 Acid Test

Table 5.14 shows the effect of sulphuric acid solution on untreated as well as on treated sandstone samples of both varieties.

5.4 DISCUSSION

The present study has shown that the average water absorption and porosity values of fresh red sandstone (RS) samples were 3.19 and 7.75 percent respectively, whereas the white spotted (WS) samples have slightly lower values of water absorption and porosity viz. 2.78 and 6.66 percent respectively. Both these properties have been found to be greatly influenced with the decay of stone. Figures 5.1, 5.2 and 5.3 and Figures 5.5, 5.6 and 5.7 clearly indicate the progressive increase of water absorption, porosity and weight loss values with the decay of stones. Further, these characteristics of the stones were found to be directly related with each other (Fig. 5.4 and 5.8). It is evident from these figures that the decaying behaviour of these stones is not uniform. The trend of deterioration was found to be quite slow in the beginning till the appearance of the cracks. In general the decaying behaviour of red sandstone has been found to be slow upto 5 cycles, after which the deterioration of the stone accelerates as shown by the steepness of the curve. The visual observations also

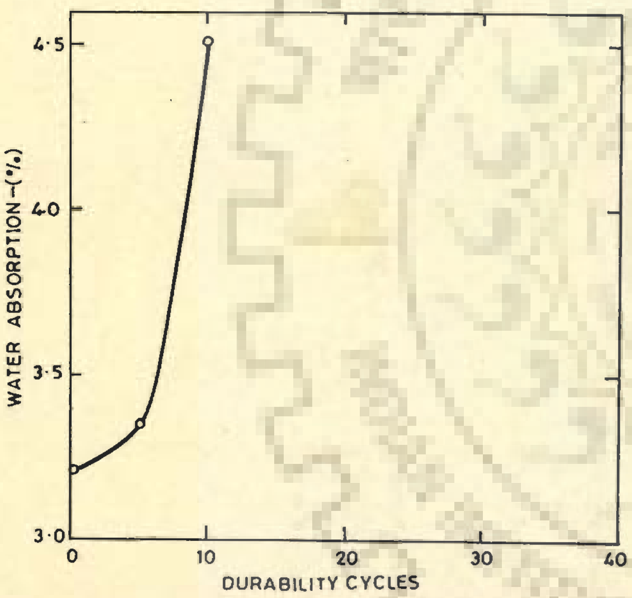


FIG. 5·1. RELATIONSHIP BETWEEN DURABILITY CYCLES & WATER ABSORPTION OF RED SANDSTONE

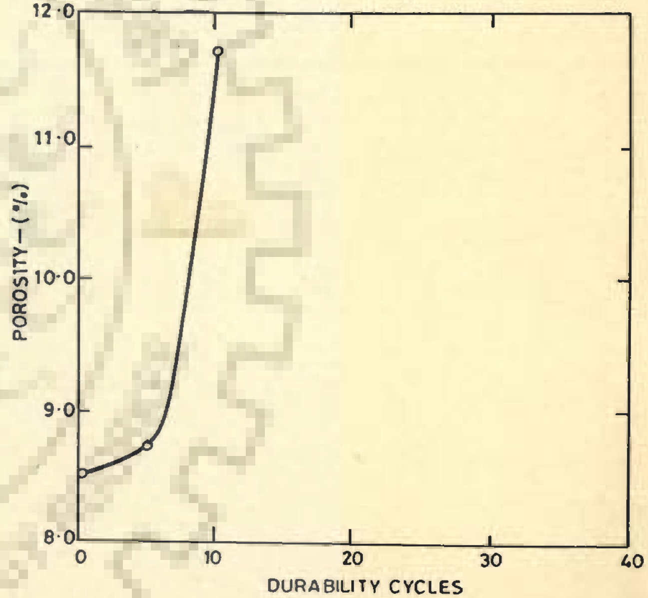


FIG. 5·2. RELATIONSHIP BETWEEN DURABILITY CYCLES & POROSITY OF RED SANDSTONE

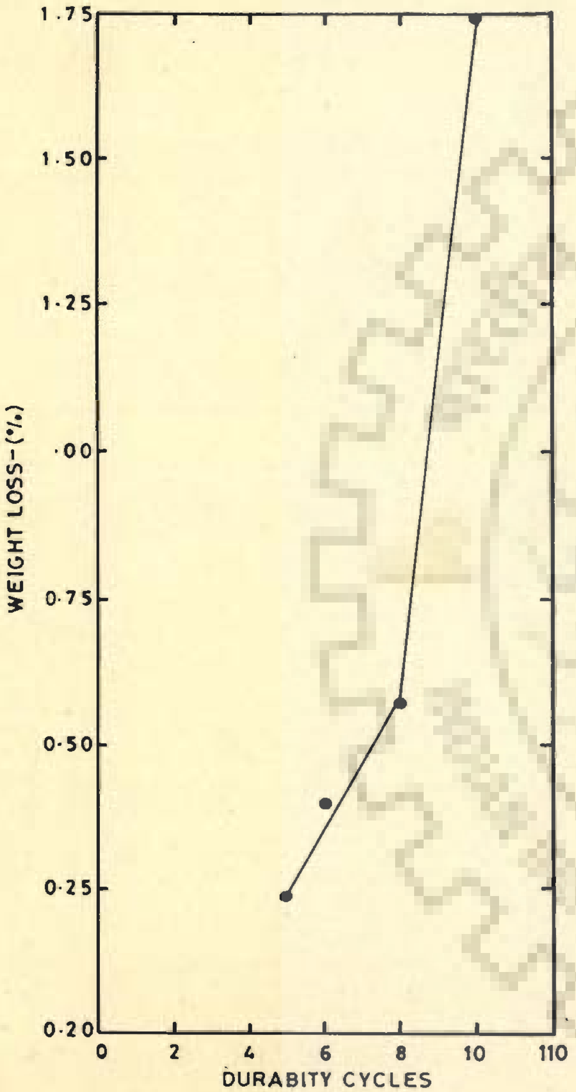


FIG.5·3. VARIATION OF WEIGHT LOSS OF RED SANDSTONE WITH DURABILITY CYCLES

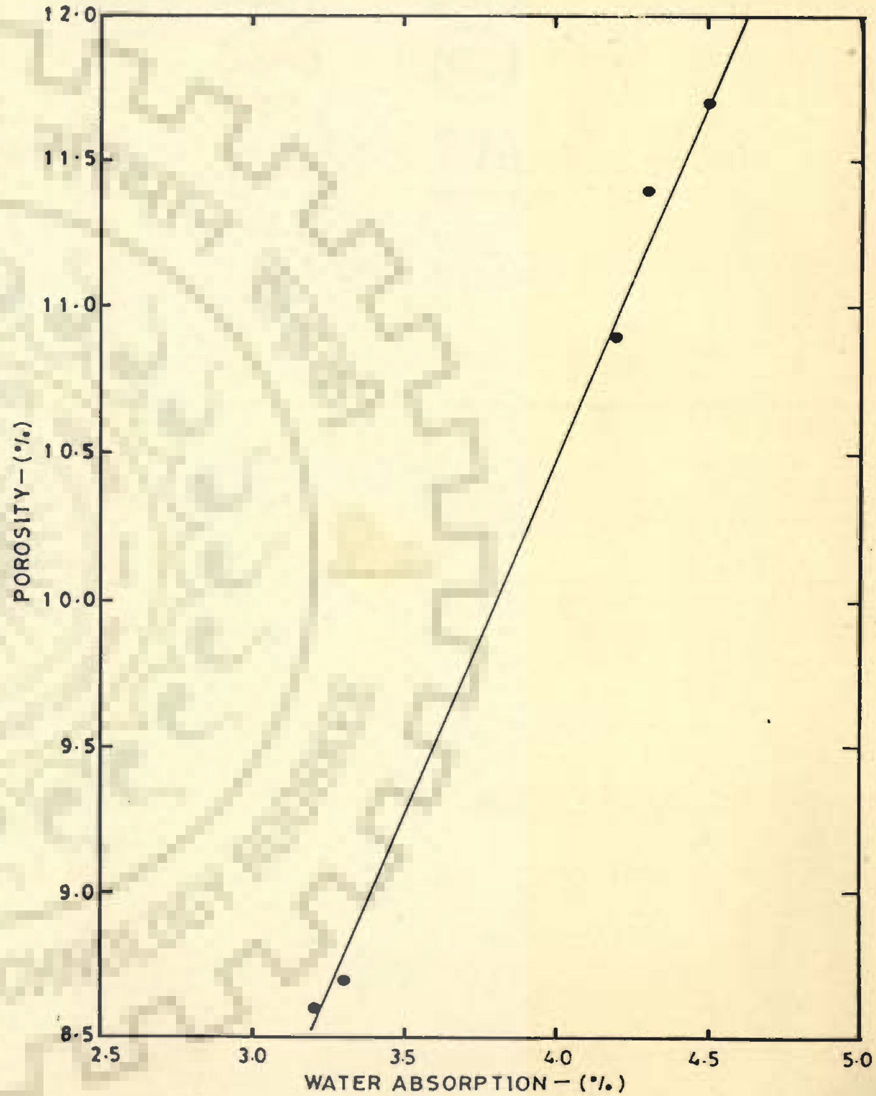


FIG.5·4. RELATIONSHIP BETWEEN POROSITY & WATER ABSORPTION OF RED SANDSTONE

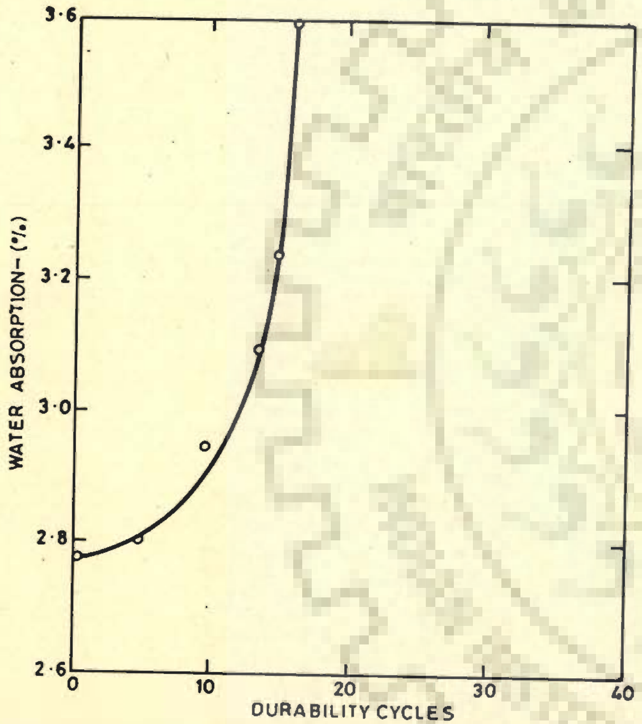


FIG. 5·5. RELATIONSHIP BETWEN DURABILITY CYCLES & WATER ABSORPTION OF WHITE SPOTTED SANDSTONE

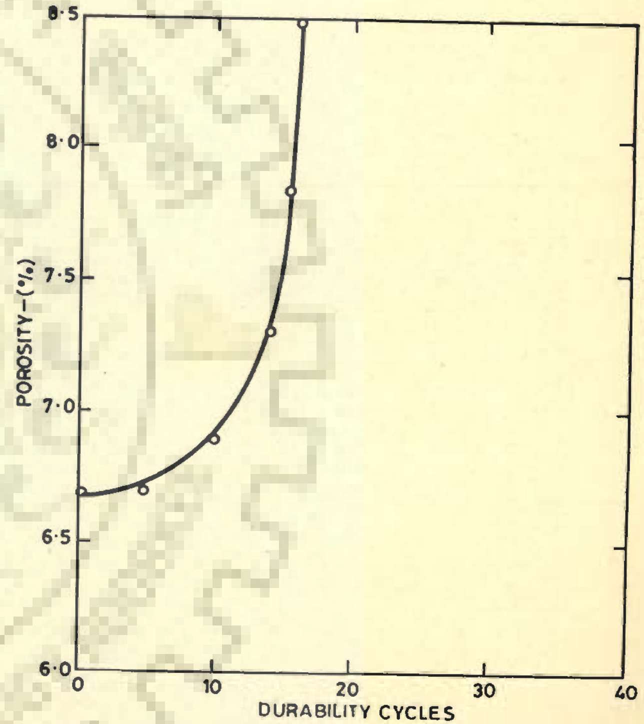


FIG. 5·6. RELATIONSHIP BETWEEN DURABILITY CYCLES & POROSITY OF WHITE SPOTTED SANDSTONE

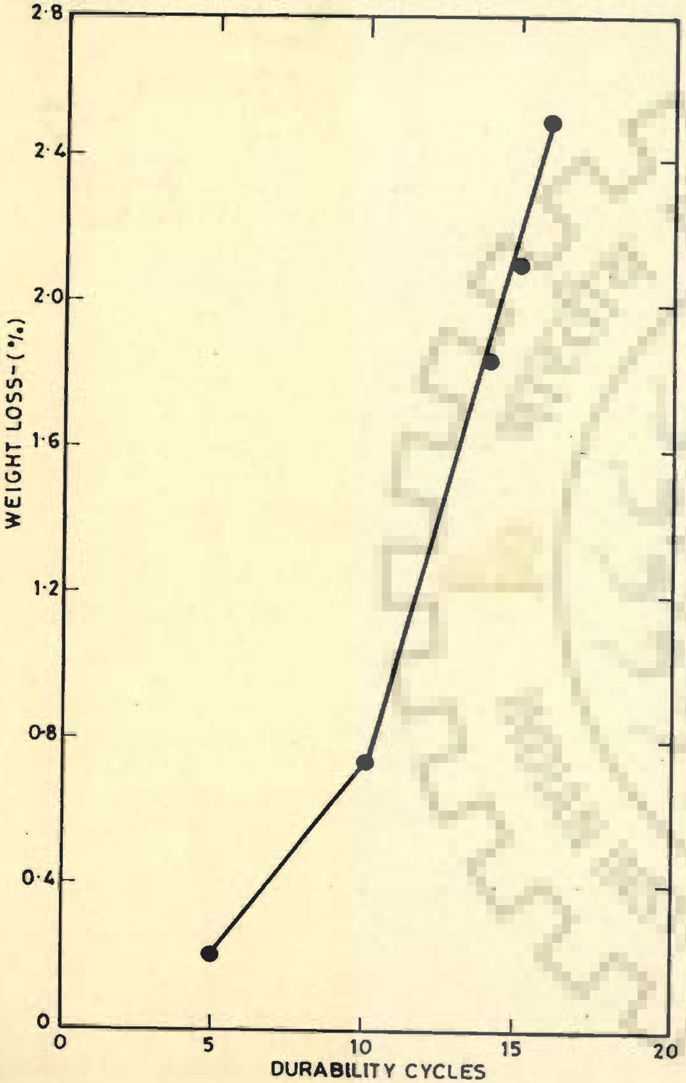


FIG.5·7. RELATIONSHIP BETWEEN DURABILITY CYCLES & WEIGHT LOSS OF WHITE SPOTTED SANDSTONE

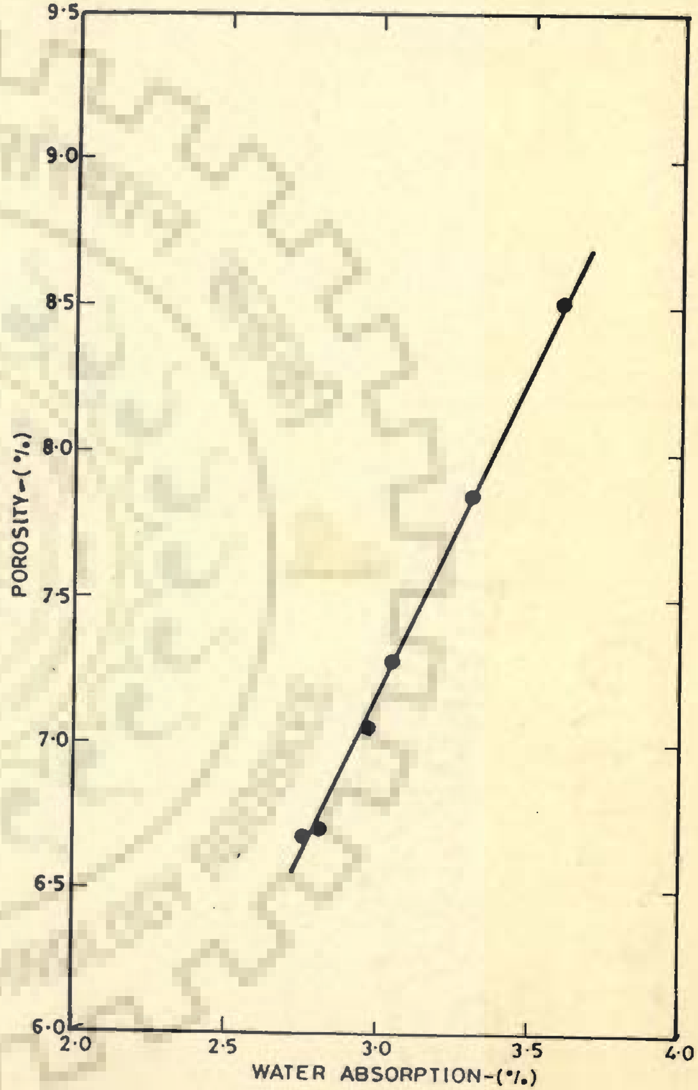


FIG.5·8. RELATIONSHIP BETWEEN POROSITY & WATER ABSORPTION OF WHITE SPOTTED SANDSTONE showed the similar trends, the samples did not show any marked sign of disintegration upto 5 cycles. The cracks appeared along the lamination of the stone after 6 cycles generally beneath the surface. These cracks widen with the number of cycles. After 10 cycles the samples get separated into pieces. The white spotted samples show more or less similar trends but they appeared to be more resistant and showed disintegration after 14-15 cycles of the durability test (Plate 5.5-5.10).

The durability behaviour of stone studied under test conditions 1,2 and 3 has exhibited (Figs. 5.9-5.12) that variation in immersion time having same concentration of solution and drying temperature i.e. 16 hrs immersion in test condition (1) and 5 hrs immersion in test condition (2) does not show any significant effect on decaying behaviour of the stone. The water absorption, porosity and weight loss values remain more or less same in both the test conditions. The change of drying temperature (test condition 3), however, has shown considerable effect on the durability behaviour. The samples of red sandstone which failed between 6-10 cycles at 105°C have failed between 17-20 cycles at 60°C drying temperature. These samples after 20 cycles of test at 60°C attained almost the same water absorption and porosity values which were found to be more or less same as under test condition (1) and (2) after 6-10 cycles. Similarly, the WS samples disintegrated between 14-16 cycles at 105°C, failed between 17-23 cycles at 60°C having more or less the same water absorption and porosity values.

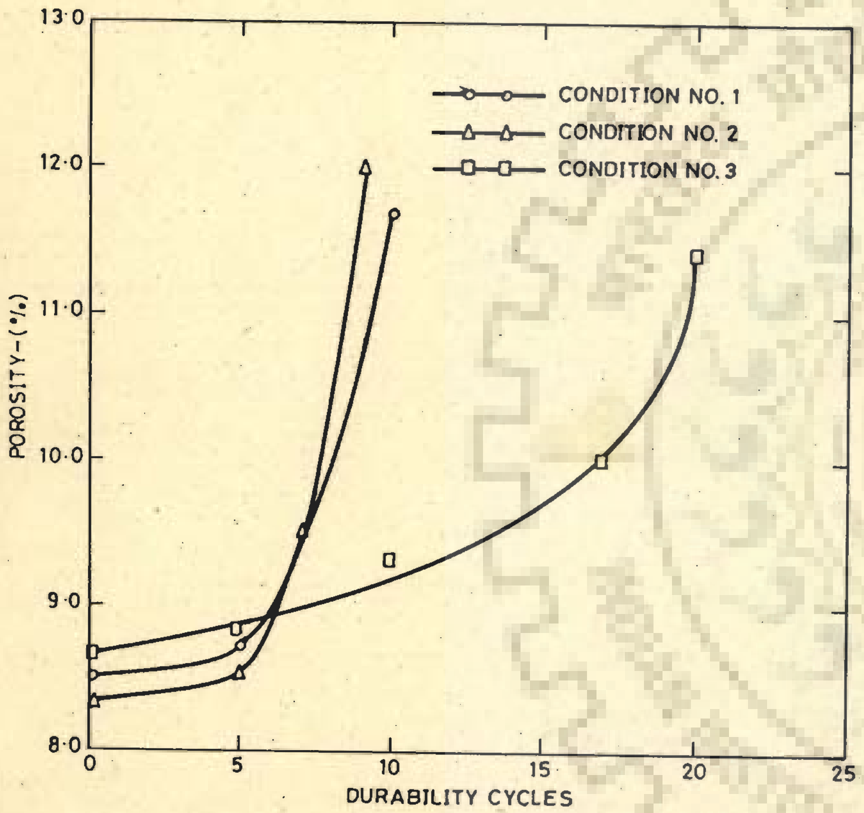


FIG. 5·9. VARIATION OF POROSITY OF RED SANDSTONE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

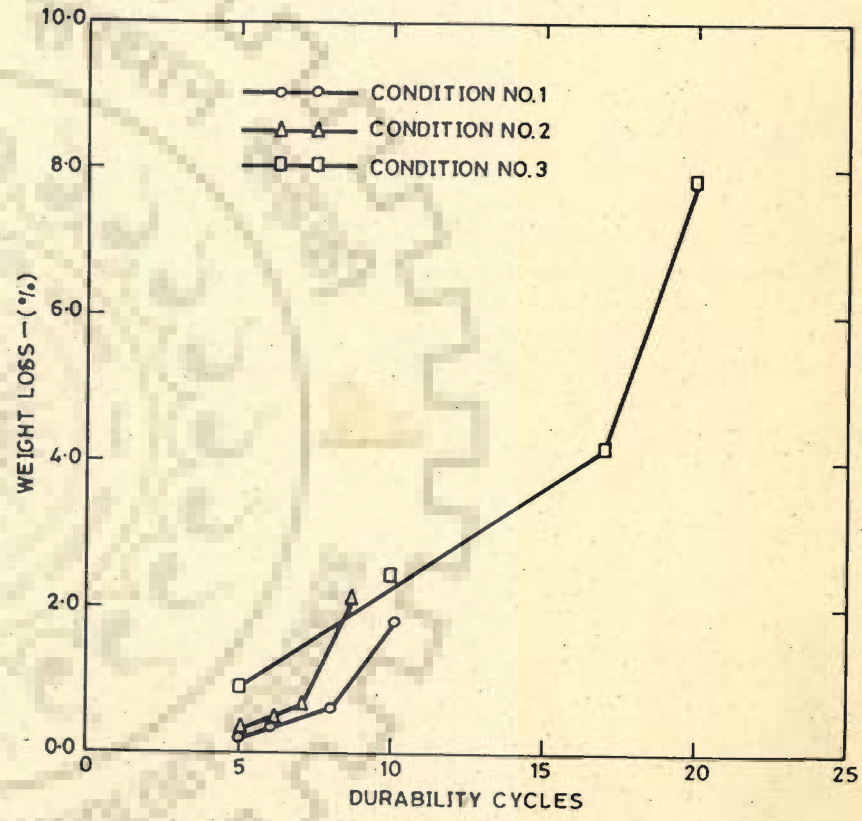


FIG. 5·10. VARIATION OF WEIGHT LOSS OF RED SAND STONE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

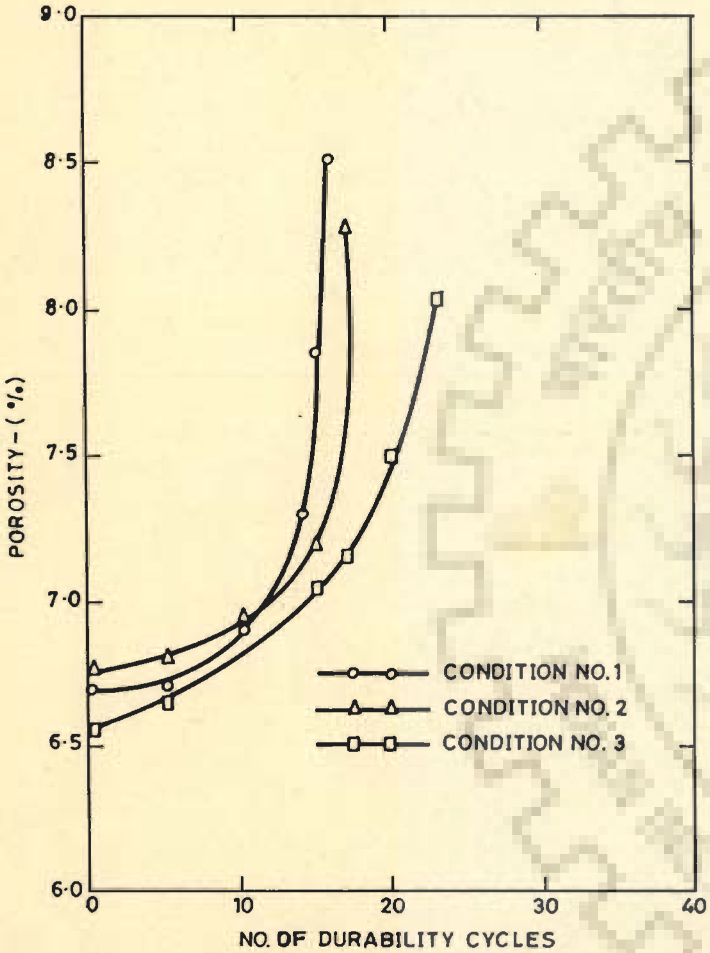


FIG.5·11. VARIATION OF POROSITY OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

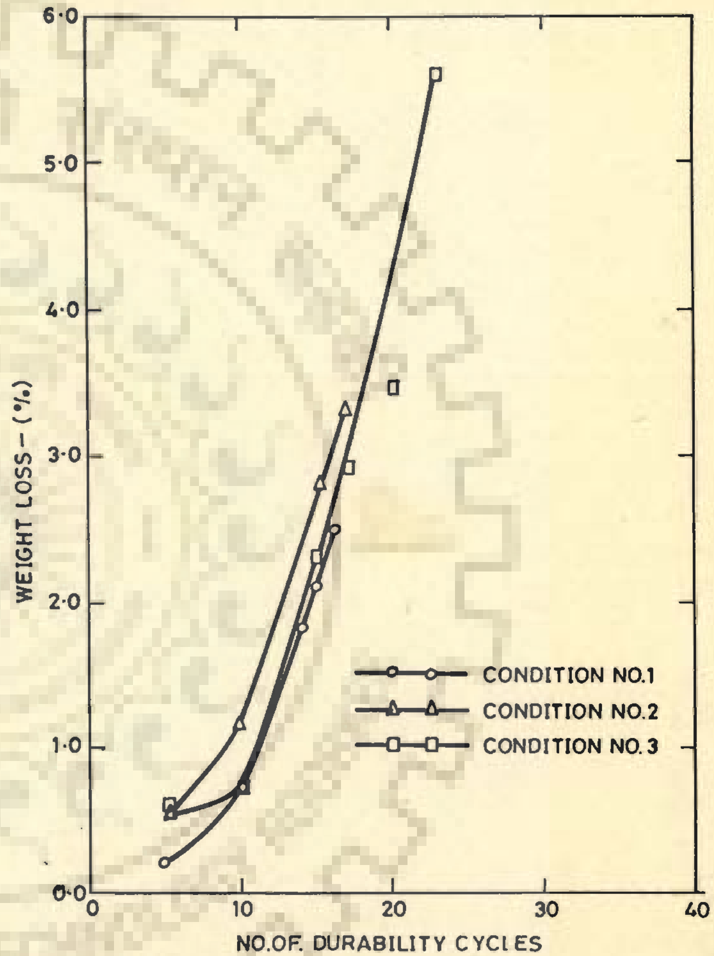


FIG.5·12. VARIATION OF WEIGHT LOSS OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

It was significant to note that the pattern of disintegration under test condition (3) was different (Plates 5.5-5.10). In this case surface roughness of the stones started after 5 cycles of the test resulting into progressive loss in weight. The possible reason for the indifferent behaviour could be slow temperature of drying. The weight loss of red sandstone under test conditions(1) and (2) was found to be 1.75 and 2.08 percent respectively, after 9-10 cycles, whereas, it was 7.81 percent after 20 cycles under test condition (3). For white spotted sandstone under test condition (1) and (2) it was 2.50 and 3.32 percent respectively after 16-17 cycles, whereas, it was 5.56 percent after 23 cycles under test condition (3).

The study thus clearly indicates that the behaviour of the stone is different under different environmental conditions rich in salts. Under severe and aggressive environmental conditions the stone deteriorates in the form of cracks otherwise the weight loss is progressive.

Further studies under microscope have revealed the pattern of decay of both the stones under durability test. In the initial stages both the sandstones have shown the loss of cementing material as well as the removal of ferrugenous coating over the silica grains. As a result the quartz grains in red sandstone become more clear and loose in the cementing material whereas in white spotted sandstone the quartz grains lack interlocking arrangement. With the advancement of durability cycles the reduction in size of silica grains occur and the cracks within the silica grains become more prominent (Plates 5.3, 5.4).

Weathering test studies showed that both the samples of sandstone pass I.S. 1125 (1974) and may be considered suitable. However, the pattern of decay of stones (Figs. 5.13 and 5.15) have been found to be somewhat peculiar as the porosity values upto 50 cycles of the test decreased possibly due to the deposition of calcium sulphate in the pores of the stones. After 50 cycles the stone starts showing decay in general as showing by increase in porosity value. It is interesting to note that the red sandstone attain the original porosity value after 90 cycles of the test and then show progressive increase in porosity values upto 100 cycles. This change in porosity has been found to be abrupt in case of white spotted sandstone (Fig. 5.15) due to the quartzite nature of this stone. The interlocking arrangement of the silica grains becomes loose causing considerable change in porosity. The same trend has been observed in the change in weights as shown in Figs. (5.14 and 5.16).

Fig. 5.17 to 5.20 showed the variation of porosity and weight loss of treated RS and WS samples respectively. The thin film of PMMA coating on the surface found to fail between 20-50 cycles of samples treated by vacuum and around 10 cycles when coated by brush. This indicates that PMMA coatings have poor adhesion on the surfaces of both varieties of sandstones. Both the stones failed around 90 cycles of the test. The dura-

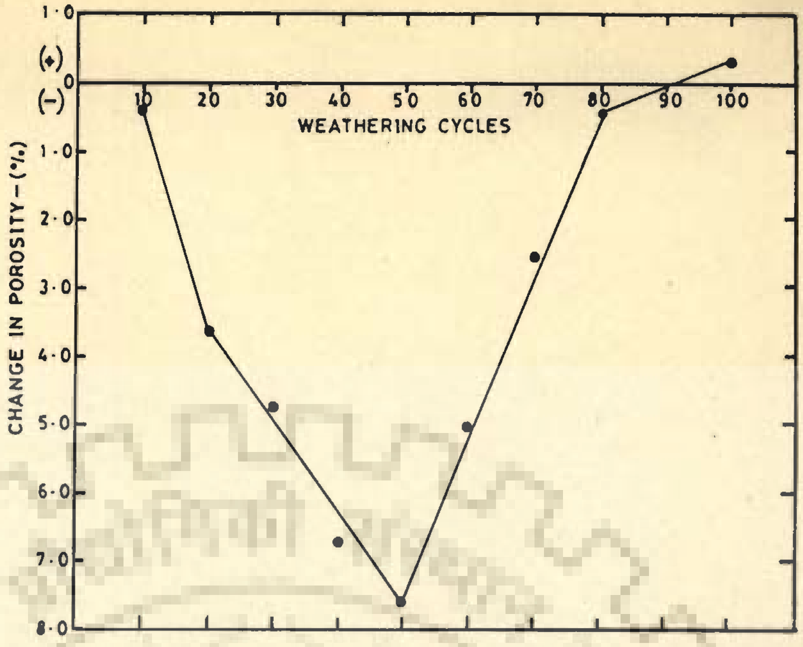


FIG. 5·13. CHANGE IN POROSITY OF RED SANDSTONE WITH WEATHERING CYCLES

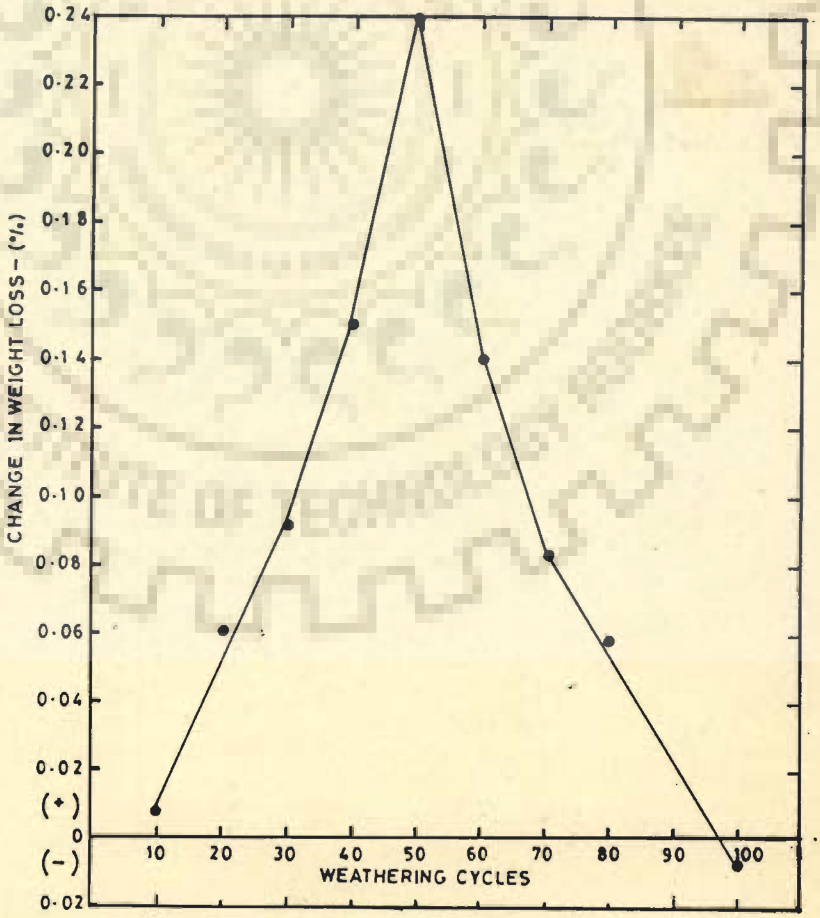


FIG. 5·14. CHANGE IN WEIGHT LOSS OF RED SANDSTONE WITH WEATHERING CYCLES

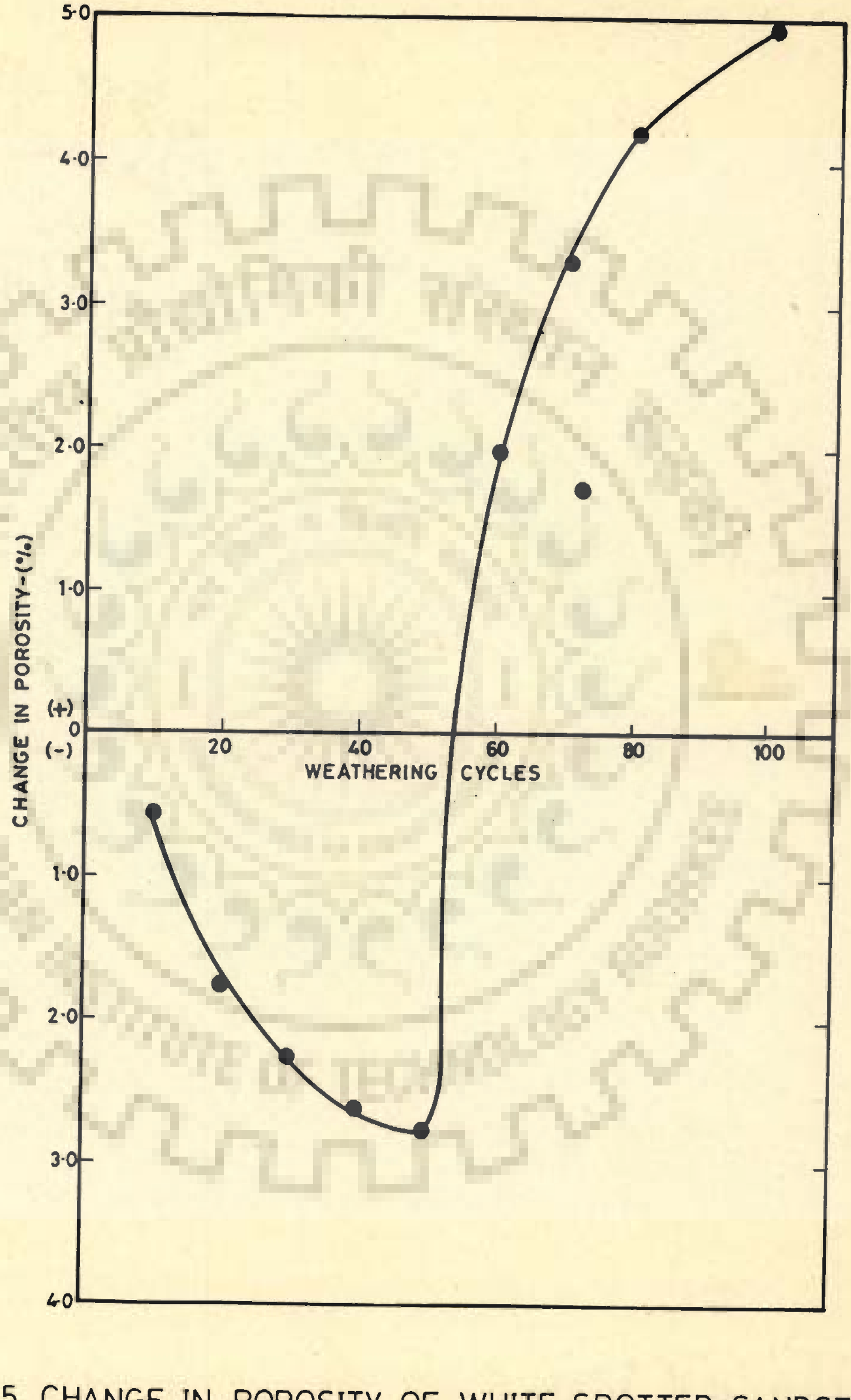


FIG.5·15. CHANGE IN POROSITY OF WHITE SPOTTED SANDSTONE WITH WEATHERING CYCLES

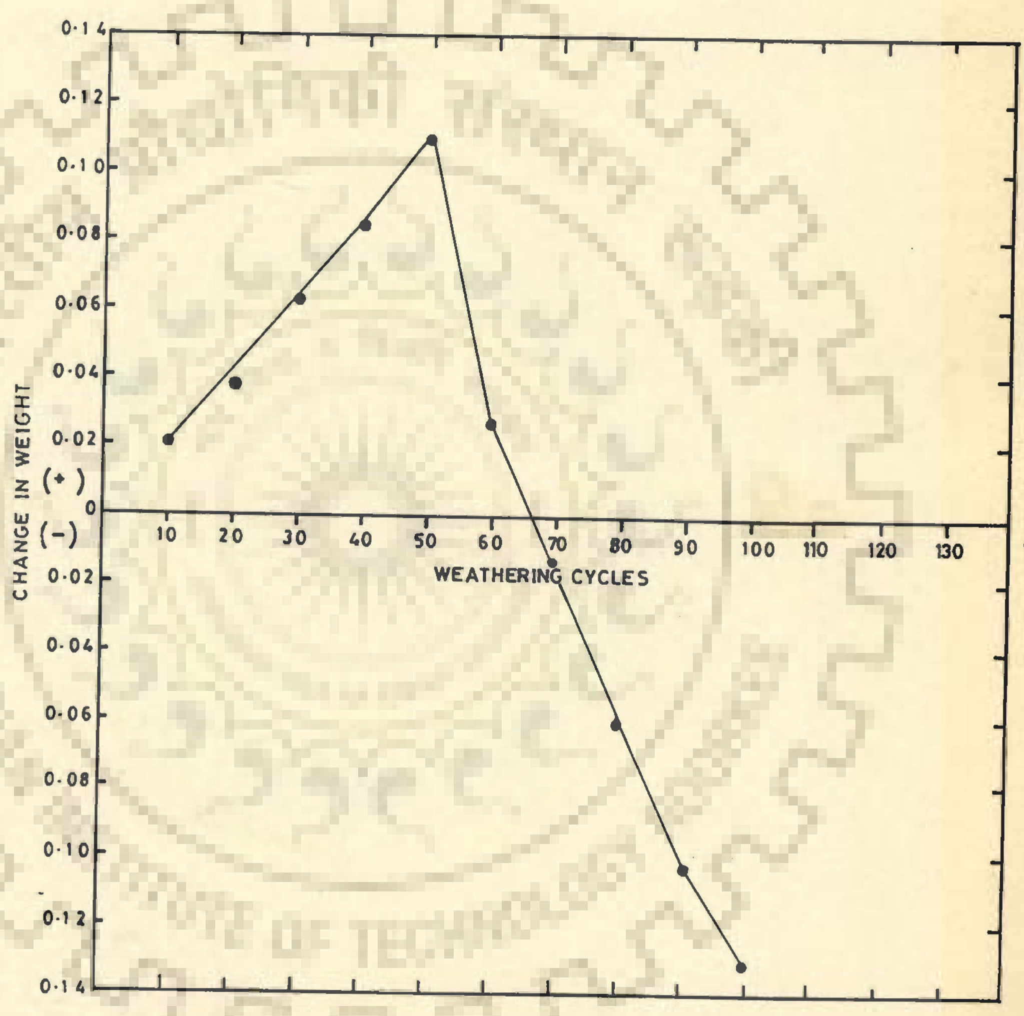
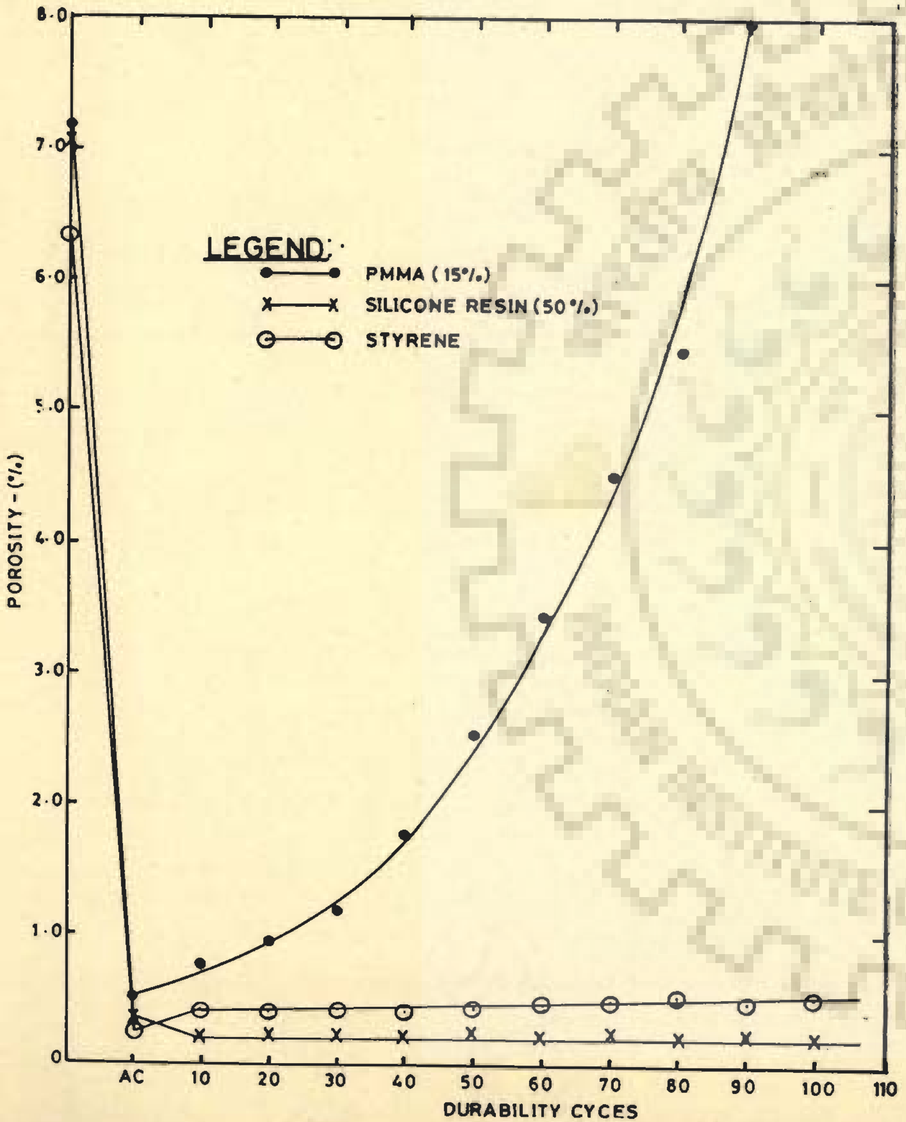


FIG.5·16.CHANGE IN WEIGHT OF WHITE SPOTTED SANDSTONE WITH WEATHERING CYCLES



G. 5·17. VARIATION OF POROSITY OF TREATED RED SANDSTONE WITH DURABILITY CYCLES

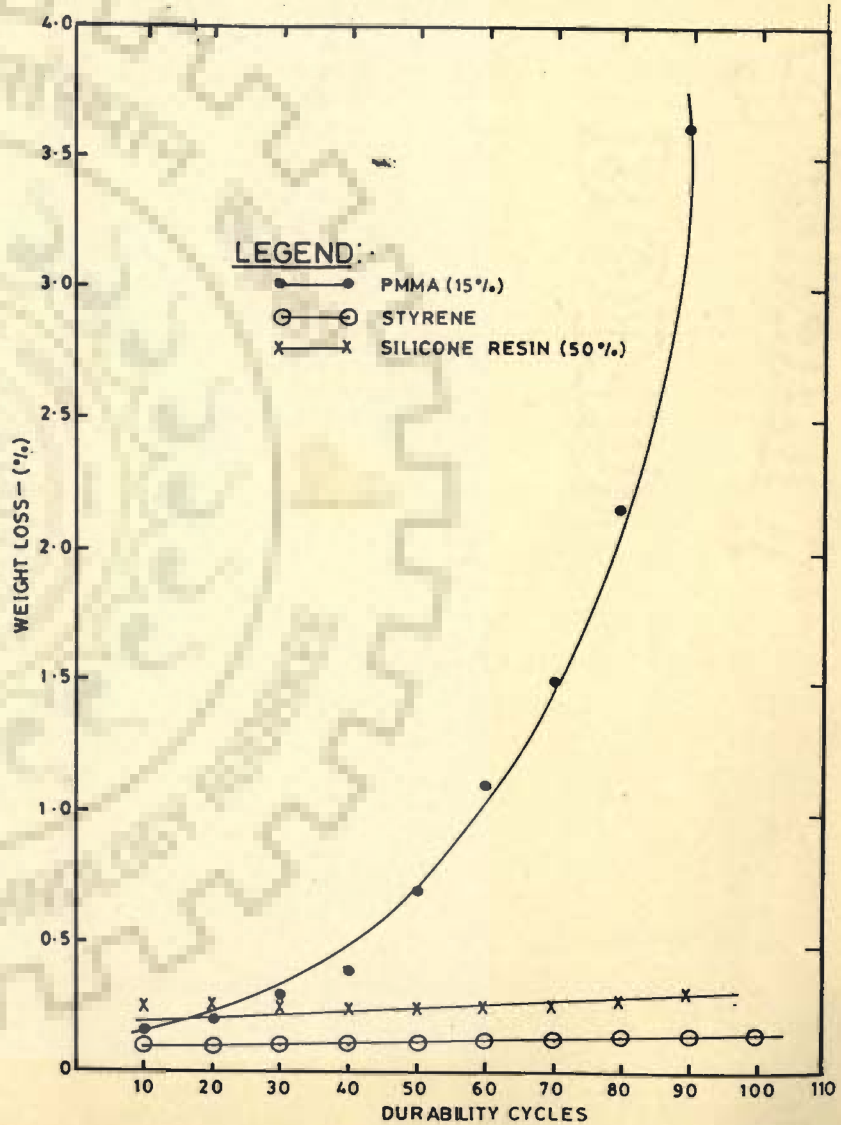


FIG. 5·18. VARIATION OF WEIGHT LOSS OF TREATED RED SANDSTONE WITH DURABILITY CYCLES

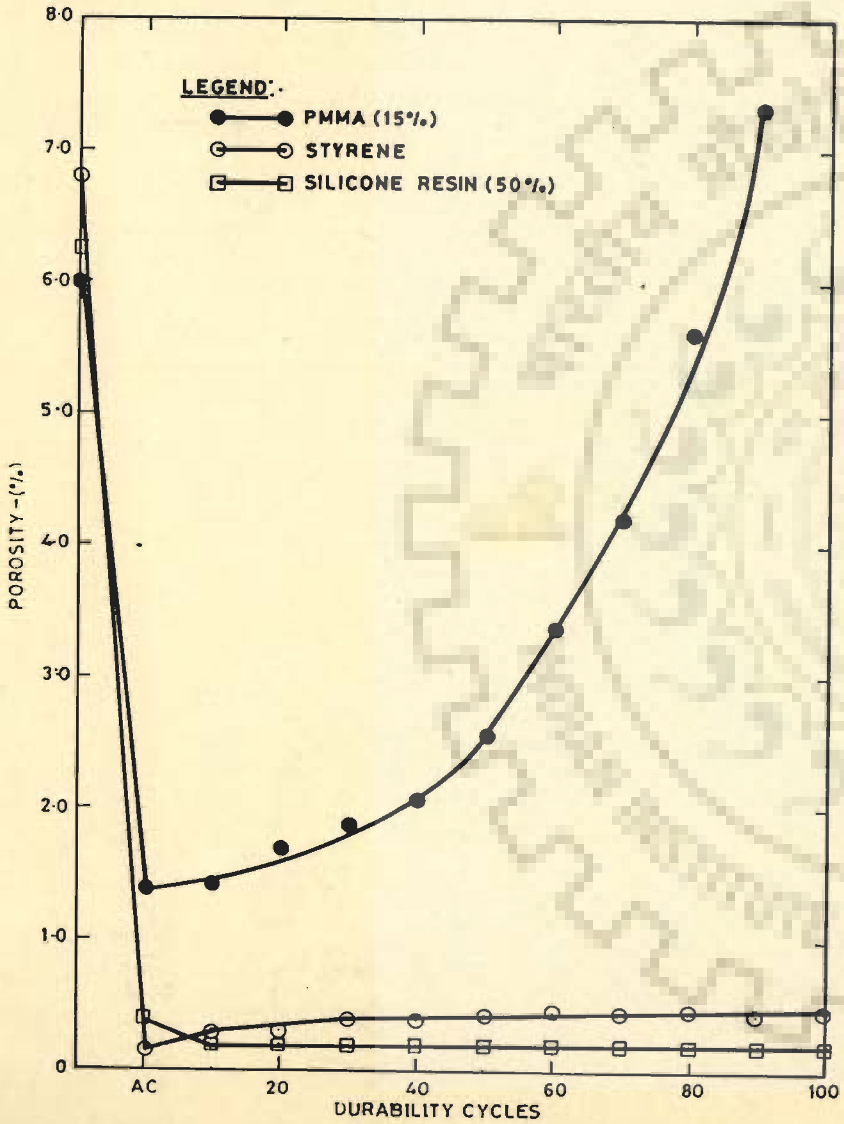


FIG.5·19. VARIATION OF POROSITY OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES

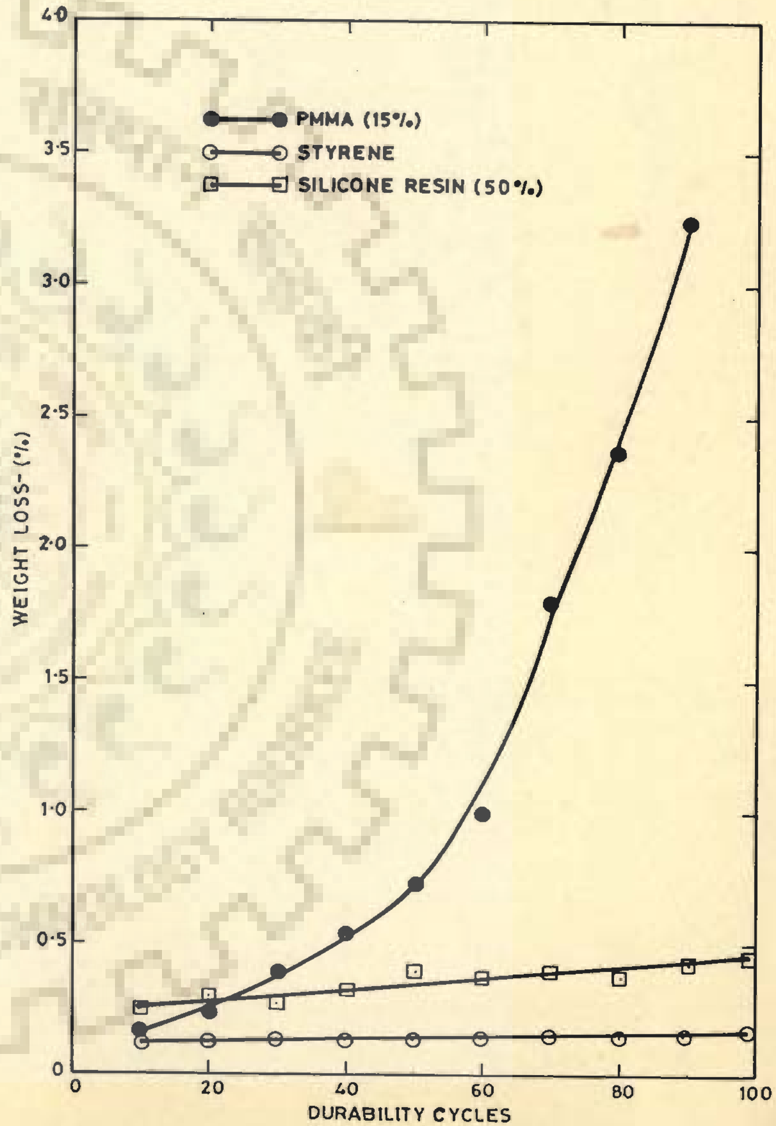


FIG.5·20. VARIATION OF WEIGHT LOSS OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES bility behaviour clearly exhibits that the life of these stones increase considerably even though the surface coating fails in earlier cycles. This shows that sufficient impregnation of PMMA resin takes place which increases the life of stones.

The treatment of RS and WS samples with styrene under vacuum also increases the life of the samples upto 100 cycles of the test. The water absorption, porosity and weight loss values were found to be very less even after 100 cycles of the test, however, the rate of decay of samples were higher than the samples treated with silicone resin.

Both RS and WS samples treated with silicone resin under vacuum did not show any sign of failure even after 100 cycles of the test. The samples also didn't show significant increase in water absorption, porosity and weight loss values after 100 cycles and so the rate of decay is minimum in this case. This could be due to the hydrophobic and consolidating nature of silicone resin.

The both varieties of sandstone treated with PMMA, styrene and silicone resin by brushing method failed around 10,20 and 40 cycles respectively. This clearly indicates that the preservative could not be impregnated deeply by brushing technique, whereas, the vacuum method results into deeper penetration of the preservatives used.

Figs.5.21 to 5.24 indicate the effect of sea water on the durability of sandstones. Untreated samples in general have shown progressive increase in porosity, water absorption

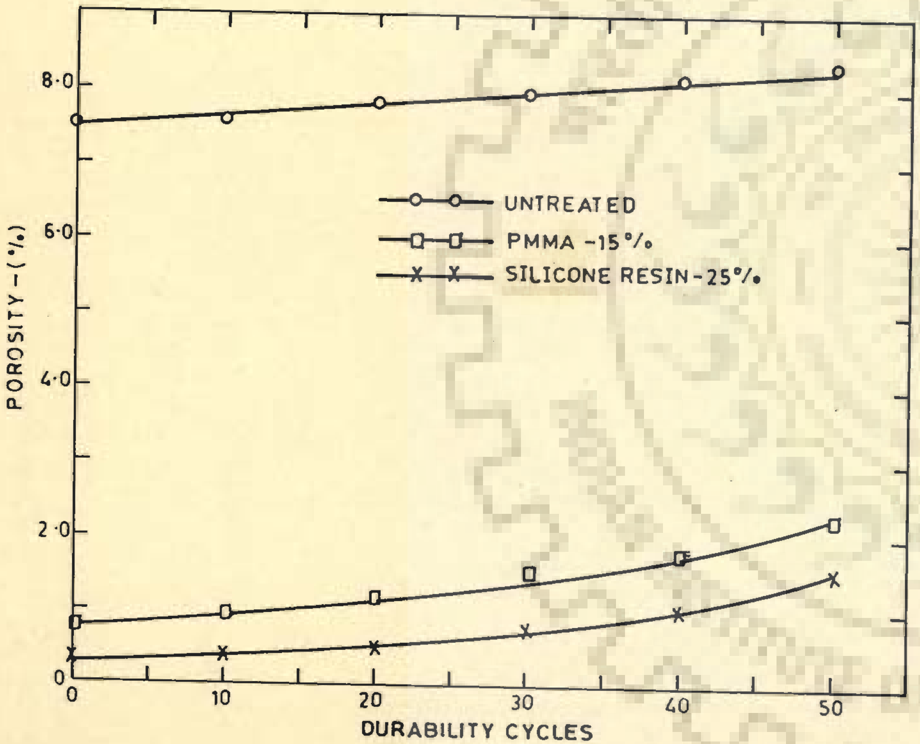


FIG.5·21. VARIATION OF POROSITY OF RED SANDSTONE WITH DURABILITY CYCLES IN SEA WATER SOLUTION

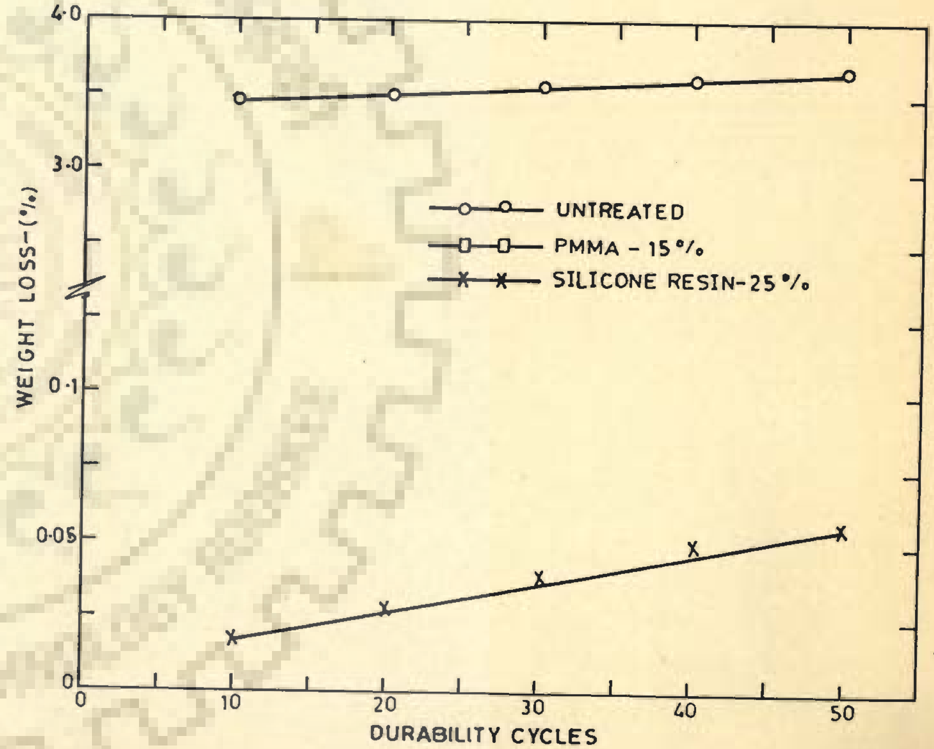


FIG.5·22. VARIATION OF WEIGHT LOSS OF RED SANDSTONE WITH DURABILITY CYCLES IN SEA WATER SOLUTION

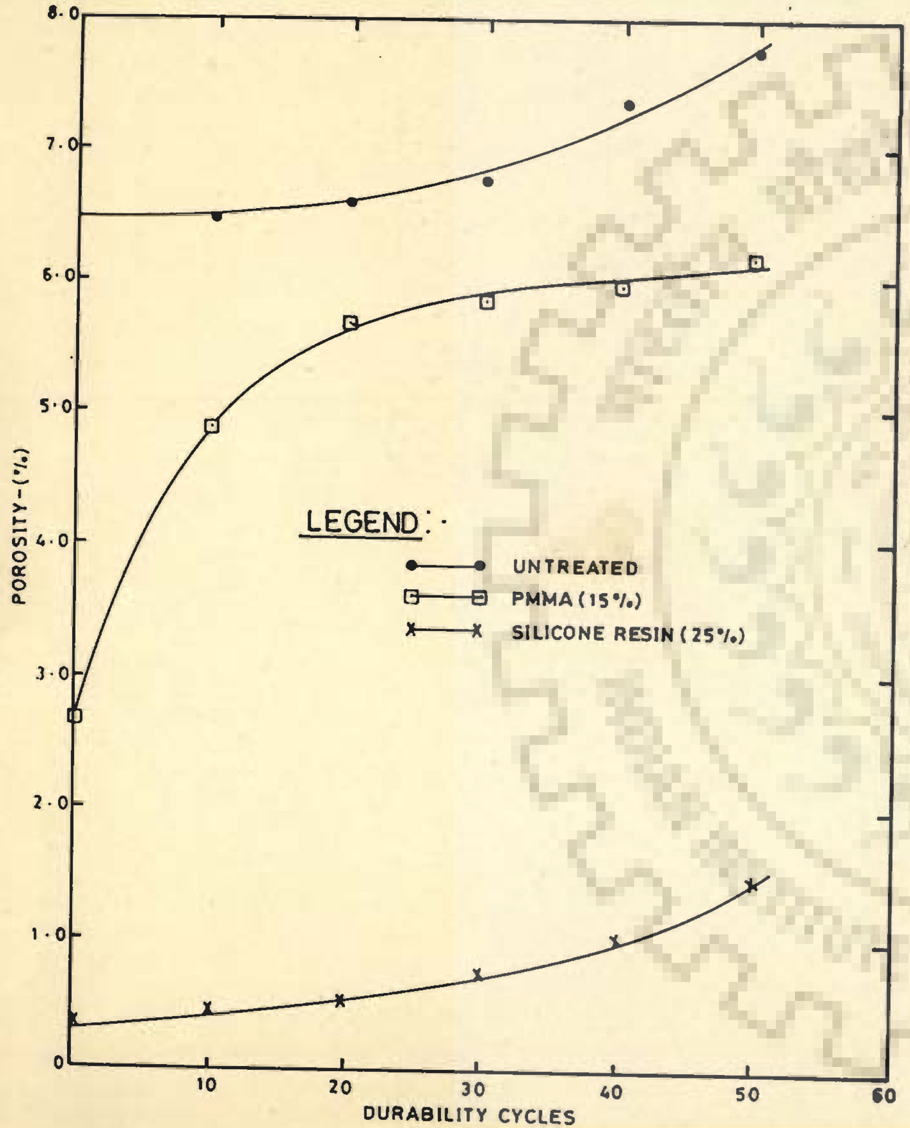


FIG. 5·23. VARIATION OF POROSITY OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES IN SEA WATER SOLUTION

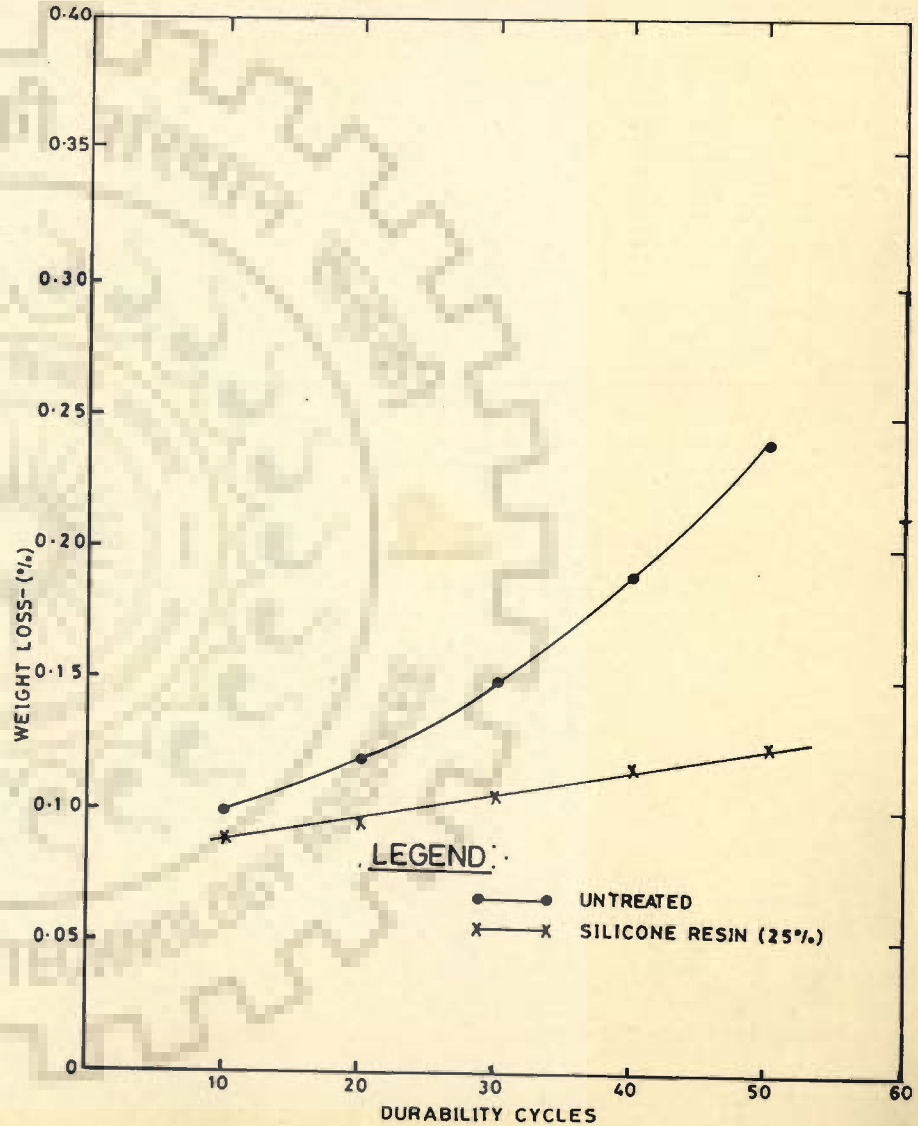


FIG. 5·24. VARIATION OF WEIGHT LOSS OF WHITE SPOTTED SANDSTONE WITH DURABILITY CYCLES IN SEA WATER SOLUTION and weight loss values. The samples did not show the formation of cracks upto the 50 cycles of the test, however, leaching of finelly crystalline matter started right from the beginning. As a result the samples loose weight progressively forming minute grooves and etched markings on the surface. The samples treated with PMMA and silicone resin show considerable reduction in the leaching of the material as well as in weight loss values.

Fig. 5.25 and 5.26 show the effect of acid environment of different concentrations on the stones. It has been observed that the extent of weight loss of the samples depends on the concentration of the acid. Higher the concentration of acid greater is the weight loss. Comparatively more loss in the case of red sandstone may be attributed to the presence of carbonates of calcium and iron in the matrix. Samples treated with PMMA have shown progressive increase in the weight loss with the increase in concentration of acid. The weight loss was found to be comparatively less than the weight loss observed in untreated stones. The behaviour of silicone resin treated stone in acid solution have shown that the weight loss was much less and samples do not show considerable increase with the increase in concentration of acid.

5.5 CONCLUSION

The present study on sandstones has revealed very significant results which are summarised below :

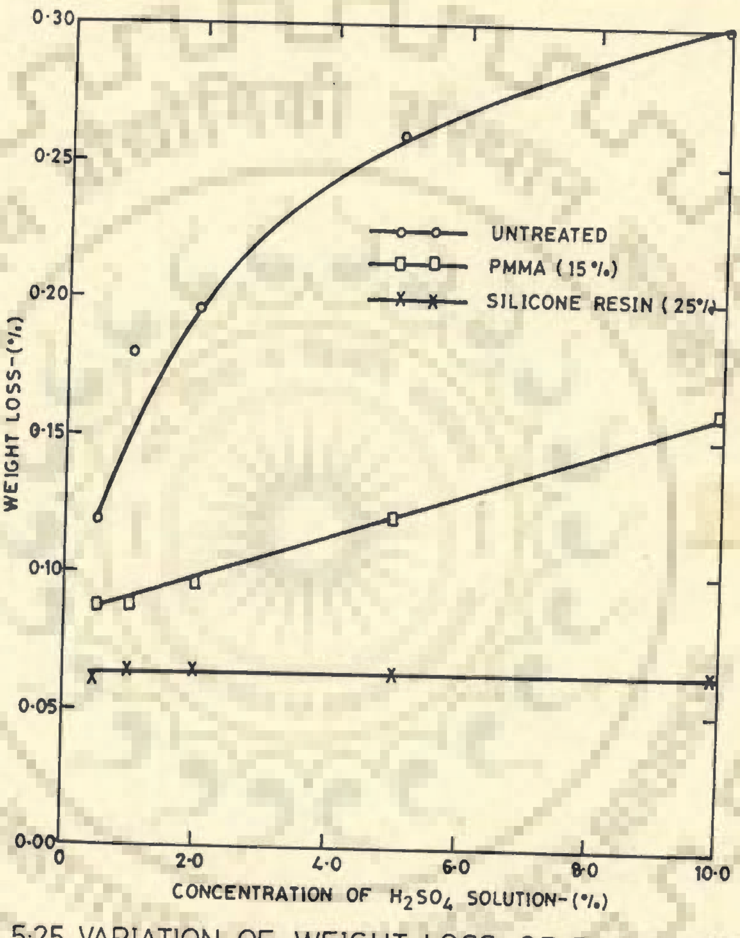


FIG.5·25. VARIATION OF WEIGHT LOSS OF RED SANDSTONE WITH CONCENTRATION OF SULPHURIC ACID SOLUTION

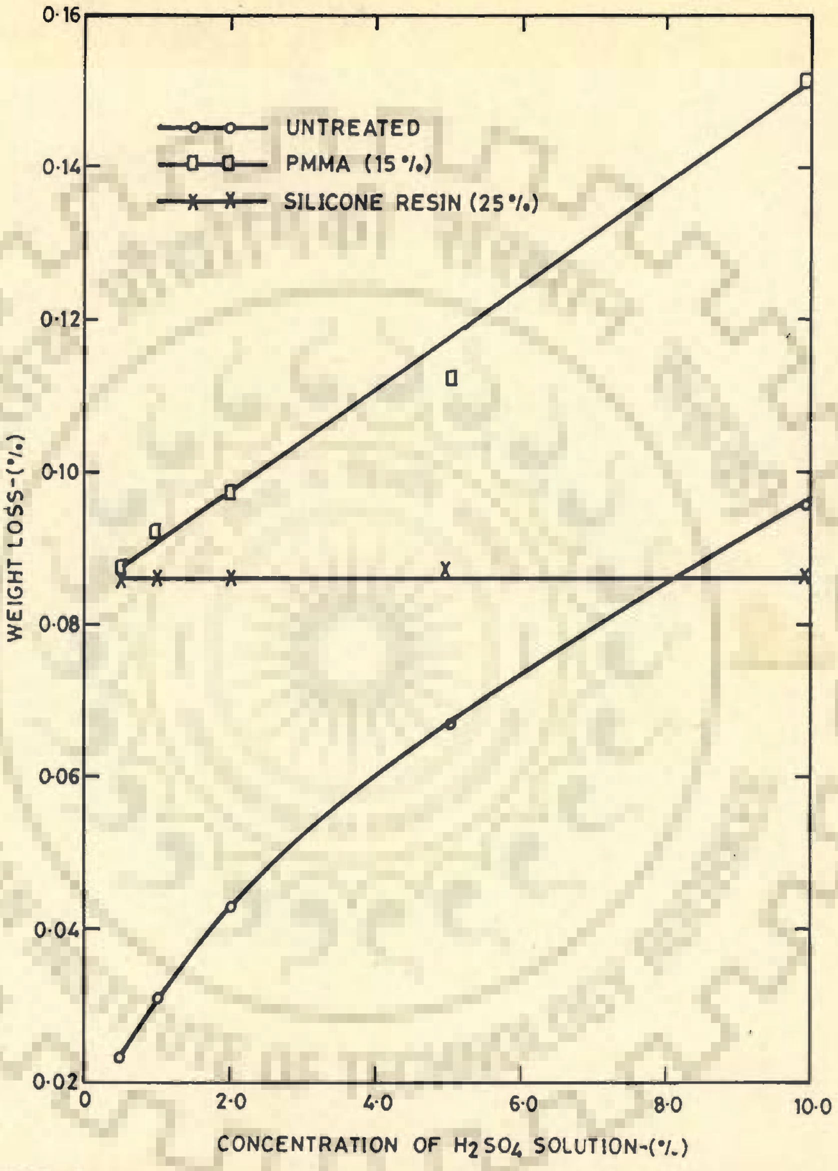


FIG. 5·26. VARIATION OF WEIGHT LOSS OF WHITE SPOTTED SANDSTONE WITH CONCENTRATION OF SULPHURIC ACID SOLUTION

1. Both varieties of stones do not pass the standard durability tests (I.S.1126, 1974) but they pass the weathering test indicating the suitability of the stones under calcium sulphate solution, corrosive ground water and temperature variation. In the durability test the samples disintegrate mostly along the bedding plane indicating unsuitability of the stones under environment rich in salts.
2. Physical characteristics of the stones e.g. water absorption, porosity and weight have been found to have direct relation with the decay of stones. All these characteristics show progressive increase with the decay of stones.
3. The deterioration of stones starts when it attains certain fixed physical properties. Among these water absorption and porosity values are the main factor on which the durability of the stones depend. For red sandstone it has been found that it disintegrates when average water absorption and porosity values became around 3.94 and 10.3 per cent respectively. For white spotted sandstone these values were found to be around 3.14 and 7.25 respectively.
4. The durability of the stones enhances considerably when preservatives are used. Among PMMA, Styrene and silicone resin, the later was found to be best for both red sandstone and white spotted sandstone under durability, seawater as well as acid environment.

CHAPTER VI

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF BASALT

CHAPTER VI

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF BASALT

6.1 INTRODUCTION

Basalt is a hard, compact, micro-crystalline to crypto-crystalline, igneous rock. It is usually dark in colour otherwise greyish to greenish black basalts are not uncommon. It is mainly composed of soda-lime felspars and ferromagnesium minerals like augite, olivine and pyroxene alongwith magnetite, biotite, apatite, hornblende and zeolites as accessory minerals. Basalts cover vast regions of central India about 51700 sq.km. in Maharashtra, Madhya Pradesh, Andhra Pradesh and Gujarat.

Basalt has been extensively used in the past for the construction of monuments, temples and caves. The famous caves of India at Ajanta, Ellora, Elephanta, Karla and Bhaja have been hewn out of basalt, which are now in various stages of deterioration. For the present study, basalt samples were collected from Elephanta caves. Survey of the area revealed that the hills consist of entirely of basalt rocks which are seldom fresh possibly due to marine environment. It is always moderate to highly weathered having moist appearance. As a result at places amygdales of the rock appeared soft material otherwise they are generally moderately hard and dark in colour. The indifferent nature of the basalt rock could be attributed to the marine environment. The sculptures made in caves too show more or less the same state of the rock. The sculptures mostly located inside the caves and which remain devoid of sunlight, appeared moderately weathered whereas those located near the entrance of the caves or close to sea-shore were generally highly weathered. The samples were collected from the detached parts of the statues as well as from the hills in which the caves are situated.

The present chapter describes the physico-chemical, mineralogical and durability behaviour of basalt. The effectiveness of preservatives namely styrene and silicone resin was also examined under different environmental conditions.

6.2 EXPERIMENTAL PROCEDURES

Samples of basalt were prepared for carrying physico-chemical, weathering and durability tests. The durability behaviour of samples treated with styrene and silicone resin (25%) were also carried out under different environmental conditions. The details of these test procedures are described in Chapter II.

6.3 RESULTS

6.3.1 Condition of Basalt Stone

In general, the condition of basalt samples were found to be highly variable. The close examination of the samples clearly indicated that the samples can be conveniently classified into two categories in terms of their visual physical conditions and appearance. In fact, the classification, clearly represents two stages of the weathering of basalt. The first category of the samples was found moderately weathered (MW) with deposition of soft clayey material in the vesicles. The second category of the samples showed considerably deterioration markings in the form of cracks and deposition of alteration materials (HW).

6.3.2 Physico-chemical Characteristics

The physical characteristic data clearly correspond to the two categories described earlier. The water absorption values of the samples were found to range from 1.0 to 1.5 and 1.6 to 2.2 percent respectively for MW and HW samples. The porosity values show variation from 3.0 to 4.5 and 4.6 to 5.9 percent for MW and HW samples respectively. The compressive strength values were found to range from 109 - 900 kg/cm^2 confirming the variation in the samples (Table-6.1).

Chemical analysis data (Table-6.1) show that the contents of the various constituents do not vary considerably indicating thereby that the leaching action to be quite poor during the decomposition of the stone. Higher loss of ignition in HW variety of the basalt indicate the decomposition of Soda-lime felspars as well as ferromagnesium minerals releasing carbonates of iron and calcium. This corresponds to the higher contents of CaO and Fe_2O_3 contents. The silica/alumina ratio has been found to vary from 3.08 to 3.77 confirming the poor leaching conditions during the course of weathering.

Table-6.1

Physico-Chemical Characteristics of Basalt

Physical Characteristics	Average Experimental Value MW	HW
Water Absorption (% by Weight)	1.0-1.5	1.6-2.2
Porosity (% by volume)	3.0-4.5	4.6-5.9
Real Density (gm/cm^3)	2.99	2.98
Bulk Density (gm/cm^3)	2.80	2.75
True Specific Gravity	2.84	2.84
Apparent Specific Gravity	2.80	2.75
Compressive Strength (Kg/cm^2)	900	109
Hardness	5-6	4-5
Chemical Analysis		
Loss of Ignition (LOI) percent	2.97	7.88
Silica (SiO_2) ''	46.46	39.41
Iron Oxide (Fe_2O_3) ''	14.64	13.50
Aluminium Oxide (Al_2O_3) ''	20.87	21.75
Calcium Oxide (CaO) ''	10.53	12.50
Magnesium Oxide (MgO) ''	4.11	3.08

6.3.3 Mineralogical Characteristics

The mineralogical studies carried out under microscope (Plate 6.1-6.3) revealed that the rock in general is moderately strong to weak both texturally and structurally. It consists predominantly of plagio-clase, felspars, ferromagnesium and iron minerals along with glassy phase. Among plagioclase labradorite has been found quite common showing lameller and carlsbad twinning of pyroxenes (augites) which occur in the ground mass and generally associated with ferrugenous material particularly along the cleavage planes or around the boundaries of the crystals. Magnetite occurs as independent grains or as inclusions in augite crystals whereas hematite is always found as coating over the ferromagnesium grains Among the glasses palagonite variety has been found.

The moderately weathered basalt has been found to consist large elongated and tabular crystals of labradorite embedded in fine to medium grained matrix rich in ferromagnesium minerals generally moderately compacted otherwise at places the grains in the matrix are separated by weathered material (Plate 6.1).

Thin section of highly weathered basalt indicated a marked reduction in the sizes of plagioclase laths as well as in the ferromagnesium minerals forming loosely compacted ground mass. Most of the grains in the matrix get coated with hematite and more weathered products are found associated with the grains (Plate 6.2).

Photomicrographs showing different stages of Basalt under durability test :

Plate (6.1) Moderate to slightly weathered basalt showing partially altered plagioclase laths of varying sizes embedded in augite plates and iron minerals (X100)

Plate (6.2) Moderate to highly weathered basalt after 10 cycles showing the development of minor cracks within the plagioclase laths- and augites having more ferrugenous stains (X200)

Plate (6.3) Rock after durability test showing highly disturbed texture with considerable reduction in the sizes of plagioclase laths and augites (X100)

Plate 6.1: Basalt Rock before Durability Test x100

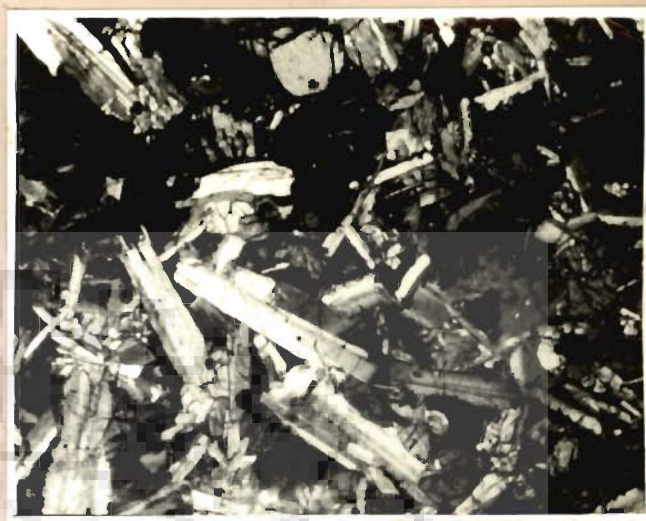


Plate 6.2: Basalt Rock after 10 cycles of durability Test x200

Plate 6.3: Basalt Rock after Durability Test x100

6.3.4 Weathering Test

Table 6.2 shows the water absorption, porosity and weight loss values of untreated basalt samples under weathering test. The water absorption and porosity values of HW samples increased from 1.60 to 2.20 and from 4.60 to 6.30 per cent respectively after 25 test cycles. The weight loss was found to be 3.70 per cent after 25 cycles. The MW samples showed the increase of water absorption and porosity values from 1.10 to 2.04 and 3.04 to 5.51 per cent respectively after 50 test cycles. The weight loss of MW samples was found to be only 2.80 per cent after 50 cycles.

3.5 Durability Test

Durability studies on untreated basalt samples were carried out under two test conditions (No. 1 and 3, Table 2.2). The variations obtained in water absorption, porosity and weight loss values of the test samples under both test conditions are shown in Table 6.3 and 6.4. It has been observed that the HW samples got disintegrated only after one test cycle under test condition (1). The water absorption and porosity values were increased from 1.94 to 2.55 and 5.06 to 6.76 per cent respectively. The samples showed maximum weight loss 11.7 per cent only after one test cycle. Under test condition (3) the HW samples of basalt disintegrated after 10 cycles with water absorption and porosity values 2.23 and 6.39 per cent respectively. The weight loss value, in this case, was 2.09 per cent after 10 cycles.

Table 6.2

Variation in Physical Characteristics of Untreated Basalt Under Weathering Test

Condition of Basalt	Initial: Water absorption (%)	Initial: Porosity (%)	No. of cycles	Final: Water absorption (%)	Final: Porosity (%)	Weight loss (%)
HW	1.60	4.60	10	1.80	5.25	2.70
			20	2.08	5.95	3.45
			25	2.20*	6.30*	3.70
MW	1.10	3.04	10	1.30	3.50	2.06
			20	1.50	4.05	2.32
			30	1.64	4.54	2.40
			40	1.90	5.11	2.60
			50	2.04	5.51	2.80

*Samples disintegrated.

Table 6.3

Variation in Physical Characteristics of Untreated Basalt Under Durability Test Condition (1)

Condition of Basalt	Initial Water absorption (%)	Initial Porosity (%)	No. of cycle	Final Water absorption (%)	Final Porosity (%)	Weight loss (%)
HW	1.94	5.06	1	2.55*	6.76*	11.7
MW	1.12	3.09	5	1.39	3.67	1.88
			10	2.0	5.14	2.59
			20	2.29	6.25	3.86
			30	2.41**	6.64**	4.09

*Samples badly disintegrated **Samples cracked

Table 6.4

Variation in Physical Characteristics of Untreated Basalt Under Durability Test Condition No.(3)

Condition of Basalt	Initial Water Absorption (%)	Initial Porosity (%)	No. of Cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)
HW	2.09	5.83	10	2.23*	6.39*	2.09
MW	1.54	4.24	20	1.64	4.70	1.28
			30	1.80	5.09	1.34
			40	1.98	5.60	1.52
			50	2.13**	6.14**	2.25

*Samples disintegrated

** Appearance of minor cracks

The MW samples having initial water absorption and porosity values 1.12 and 3.09 percent respectively have undergone 30 test cycles before they got disintegrated under test condition (1). The water absorption and porosity values of the stones after 30 cycles were found to be 2.41 and 6.64 per cent respectively and weight loss 4.09 percent. Under test (3) the MW samples having 1.54 and 4.24 percent water absorption and porosity respectively showed the appearance of minor cracks after 50 test cycles having 2.13 percent water absorption and 6.14 percent porosity. The weight loss was found to be 2.25 percent after 50 test cycles.

The variation in water absorption, porosity and weight loss values after treatment with styrene and silicone resin are shown in Table 6.5 and 6.6. The variation in these properties of untreated as well as treated are concised in Table 6.7.

The treatment with styrene under vacuum reduced the water absorption and porosity values of HW basalt samples from 2.15 to 1.24 and from 5.90 to 3.54 percent respectively. These samples showed disintegration after 13 cycles having water absorption and porosity values 2.32 and 6.53 percent respectively and weight loss 3.76 percent.

The water absorption and porosity values of MW samples reduced from 1.54 to 0.70 and 4.50 to 2.02 percent respectively after the treatment. After 30 cycles of the durability test the treated samples attained almost the initial physical

Table 6.5

Variation in Physical Characteristics of Styrene Treated Basalt under Durability Test(3)

Condition of Basalt	Initial Water Absorption (%)	Initial Porosity (%)	After coating Water Absorption (%)	After coating Porosity (%)	No. of Cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)
HW	2.15	5.90	1.24	3.54	13	2.32*	6.53*	3.76
MW	1.54	4.50	0.70	2.02	10	1.35	3.60	0.49
					20	1.50	4.06	1.13
					30	1.70	4.49	1.37
					40	1.84	4.94	1.61
					50	1.99	5.30	1.80
					60	2.15	5.77	2.06
					70	2.31*	6.22*	2.30

*Samples disintegrated

Table 6.6

Variation in Physical Characteristics of Silicone Resin treated Basalt Under Durability Test(3)

Condition of Basalt	Initial Water Absorption (%)	Initial Porosity (%)	After coating Water Absorption (%)	After coating Porosity (%)	No. of cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)
HW	1.92	5.16	1.04	2.90	20	2.0*	6.17*	2.06
MW	1.11	3.08	0.44	1.18	10	0.837	2.29	0.850
					20	1.00	2.65	0.970
					30	1.10	2.90	1.12
					40	1.20	3.05	1.20
					50	1.24	3.20	1.30
					60	1.26	3.25	1.49
					70	1.30	3.39	1.60

*Samples disintegrated

Table-6.7

Durability Behaviour of Basalt

Untreated/ Treated	Test condition	Sample	Initial		After Coating		Disintegration Cycle	Final		Weight loss	Rate of Decay (Wt.loss/ cycle)
			Water Absorption (%)	Porosity (%)	Water Absorption (%)	Porosity (%)		Water Absorption (%)	Porosity (%)	(%)	
Untreated	(1)	HW	1.94	5.06	-	-	1	2.55	6.76	11.7	11.7
		MW	1.12	3.09	-	-	30	2.41	6.64	4.09	0.136
	(3)	HW	2.09	5.83	-	-	10	2.23	6.39	2.09	0.209
		MW	1.54	4.24	-	-	50	2.13	6.14	2.25	0.045
Styrene	(3)	HW	2.15	5.90	1.24	3.54	13	2.32	6.53	3.76	0.289
		MW	1.54	4.50	0.70	2.02	70	2.31	6.22	2.30	0.033
Silicone Resin(25%)	(3)	HW	1.92	5.16	1.04	2.90	20	2.00	6.17	2.06	0.103
		MW	1.11	3.08	0.44	1.18	70*	1.30	3.39	1.60	0.023

*Samples not disintegrated

values and afterwards the behaviour of the samples were found as observed in untreated samples. After 70 cycles the samples developed cracks having water absorption and porosity values 2.31 and 6.22 percent respectively. The weight loss value was found to be 2.30 percent after 70 cycles.

The treatment with silicone resin under vacuum reduced the water absorption and porosity values of HW samples from 1.92 to 1.04 and 5.16 to 2.90 percent respectively. The samples showed disintegration after 20 cycles having 2.0 and 6.17 percent water absorption and porosity values respectively. The weight loss was found to be 2.06 percent.

The treatment of MW samples reduced the water absorption and porosity values from 1.11 to 0.44 and 3.08 to 1.18 percent respectively. After 40 test cycles, the MW samples attained more or less similar to the initial values. The samples didn't disintegrated after 70 cycles and show 1.30, 3.39 and 1.60 percent water absorption, porosity and weight loss values respectively.

6.3.6 Sea Water Test

The HW samples having 2.20 and 5.90 percent water absorption and porosity respectively got badly disintegrated within 4 to 7 cycles showing 2.38 percent weight loss. The MW samples disintegrated after 50 test cycles having 2.17, 5.74 and 2.0 percent water absorption, porosity and weight loss respectively (Table 6.8).

The HW samples treated with styrene got disintegrated after 10 cycles. The water absorption and porosity values were

Table 6.8

Variation in Physical Characteristics of Untreated Basalt under Sea Water Test

Condition of Basalt	Initial Water Absorption (%)	Initial Porosity (%)	No. of Cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)
HW	2.20	5.90	4-7*	-	-	2.38
MW	1.13	3.12	10	1.30	3.50	0.40
			20	1.50	4.06	0.752
			30	1.75	4.50	1.09
			40	1.95	5.0	1.58
			50	2.17**	5.74**	2.00

*Samples badly disintegrated
**Appearance of cracks

Table 6.9

Variation in Physical Properties of Styrene treated Basalt Under Sea-Water Test

Condition of Basalt	Initial Water Absorption (%)	Initial Porosity (%)	After coating Water Absorption (%)	After coating Porosity (%)	No. of cycle	Final Water Absorption (%)	Final Porosity (%)	Weight loss (%)
HW	1.80	4.80	1.04	2.90	10	2.50*	6.50*	2.40
MW	1.30	3.45	0.590	1.55	10	1.15	2.90	0.40
					20	1.28	3.30	0.70
					30	1.40	3.70	1.05
					40	1.55	4.00	1.40
					50	1.70	4.45	1.75

*Samples disintegrated

found to increase from 1.04 to 2.50 and 2.90 to 6.50 percent respectively. The MW samples didn't fail after 50 cycles having 1.70, 4.45 and 1.75 percent water absorption, porosity and weight loss respectively (Table 6.9).

The HW basalt samples treated with silicone resin disintegrated after 17 test cycles showing 2.30, 6.40 and 2.30 percent water absorption, porosity and weight loss respectively. The MW samples didn't fail after 50 test cycles having only 1.25, 3.25 and 1.0 percent water absorption, porosity and weight loss respectively (Table 6.10).

6.3.7 Acid Test

Table 6.11 clearly indicates that the effect of H_2SO_4 solution on untreated samples increases with the concentration of H_2SO_4 solution. The samples showed 1.13 percent to 3.18 percent weight loss with 0.5 to 10.0 percent concentration of H_2SO_4 solution.

The test showed the leaching of material into the acid solution. The qualitative analysis of the solution of each concentration shows the presence of iron, magnesium and also calcium (intraces). The dark black colour of basalt samples after ten days immersion became dull and white spots at the points of pits appeared on the surface, which increased with higher concentration of acid.

6.4 DISCUSSION

The results obtained from this study have clearly indicated the presence of two categories of basalts. The initial physical characteristics of the stone shows the extent of

Table 6.10

Variation in Physical Properties of Silicone Resin Treated Basalt Under Sea Water Test

Condition of Basalt	Initial		After coating		No. of cycle	Final		
	Water Absorption (%)	Porosity (%)	Water Absorption (%)	Porosity (%)		Water Absorption (%)	Porosity (%)	Weight loss (%)
HW	1.98	5.20	1.00	2.80	17	2.30*	6.40*	2.30
MW	1.20	3.12	0.476	1.19	10	0.80	1.90	0.20
					20	1.0	2.40	0.40
					30	1.15	2.80	0.60
					40	1.20	3.05	0.80
					50	1.25	3.25	1.0

*Samples disintegrated

Table 6.11

Behaviour of Untreated Basalt Under Acid Test

Concentration of H_2SO_4 Sol. (% V/V)	Weight Loss (%)
0.5	1.13
1.0	1.70
2.0	2.20
5.0	2.68
10.0	3.18

weathering stone has suffered. Based on these observations as well as the performance of the stone under durability and weathering tests the samples easily be grouped into two categories marked highly weathered (HW) and moderately weathered (MW). The study has clearly pointed out the behaviour of the existing state of stones in terms of their life span.

Durability test results revealed that the behaviour of the stones is dependent on the extent of weathering they have suffered related to the compactness and hardness of the stones. The HW samples badly failed in one cycle under test condition(1) (Plate 6.4) whereas the samples of same group could understood 10 cycles under test condition (3). Similar trend has been observed for MW basalt under both the tests (Fig. 6.1). These samples showed failure after 30 cycles under test condition (1) (Plate 6.5) whereas the samples of same group understood 50 cycles under test condition (3). The study showed very significant result that both types of the stones failed after attaining the physical characteristics, water absorption and porosity values, within 2.0 to 2.50 and 6.10 to 6.80 percent respectively.

The study has clearly shown that the disintegration of basalt samples under weathering, durability and sea-water tests starts with the leaching of material filled in the pores (amygdals) of the stone forming grooves and pits over the surface of stone along with the appearance of brown ferrugenous material. The degree of disintegration of the stone can be assessed with the presence of brownish material over the surface which could be the weathered product released from the

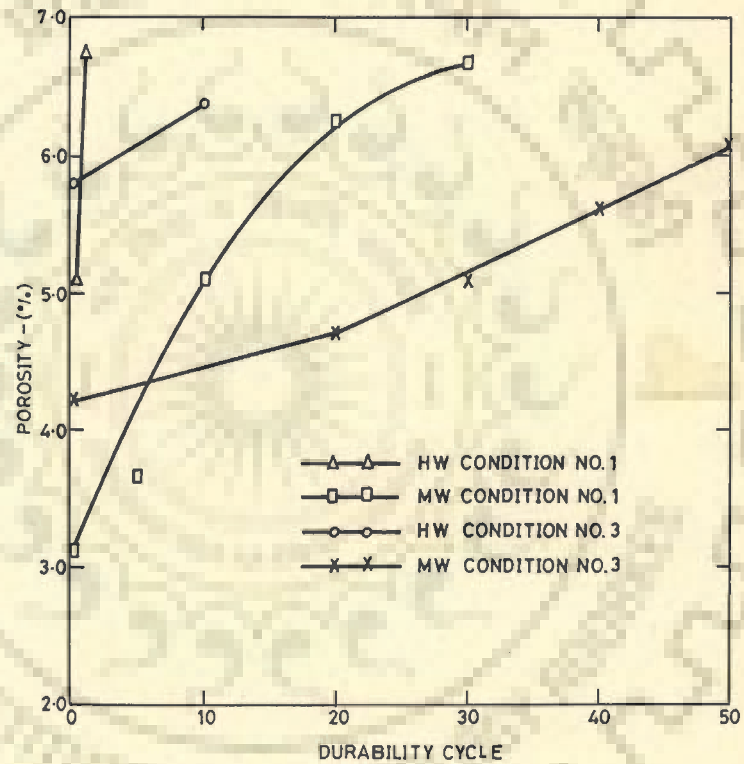


FIG. 6·1. VARIATION OF POROSITY OF UNTREATED BASALT WITH DURABILITY CYCLES UNDER DIFFERENT TEST CONDITIONS

Plate 6.4: Highly weathered Basalt after 1 cycle

Plate 6.5: Moderately Weathered Basalt after 30 cycles

Plate 6.6: Moderately weathered Basalt treated with Silicone Resin after 70 cycles

Plate 6.7: Moderately Weathered Basalt treated with Styrene after 70 cycles

weathering of ferromagnesiam mineral. It has been observed that during the tests the weathered product in the form of brownish material increases progressively.

The behaviour of stones treated with styrene and silicone resin under durability test have clearly shown the effectiveness of the preservatives. The styrene treated samples showed the improvement in the durability of both HW and MW basalt samples. The former failed after 13 cycles and the later after 70 cycles. In comparison to this the HW samples treated with silicone resin failed after 20 cycles and MW samples did not fail even after 70 cycles (Fig. 6.2 and 6.3). The physical characteristics and photomacrographs (Plate 6.6, 6.7) clearly indicated the effectiveness of the preservative. The silicone based resin therefore may be considered to be the most effective preservative for the conservation of this stone. The physical characteristics of the treated samples at the point of failure has been found to lie in the same range as observed in the durability tests of untreated samples.

Weathering test results on untreated basalt samples have clearly indicated that the behaviour of the stone depend entirely on the initial physical characteristics of the stone. The HW basalt samples failed after 25 test cycles of weathering whereas the MW basalt samples did not show any significant sign of disintegration even after 50 cycles of weathering (Fig. 6.4). The pattern of disintegration has been found to be the same as observed in the durability studies i.e. loss of amygdals and formation of pits lead up to progressive loss of weight and increase in porosity and water absorption values.

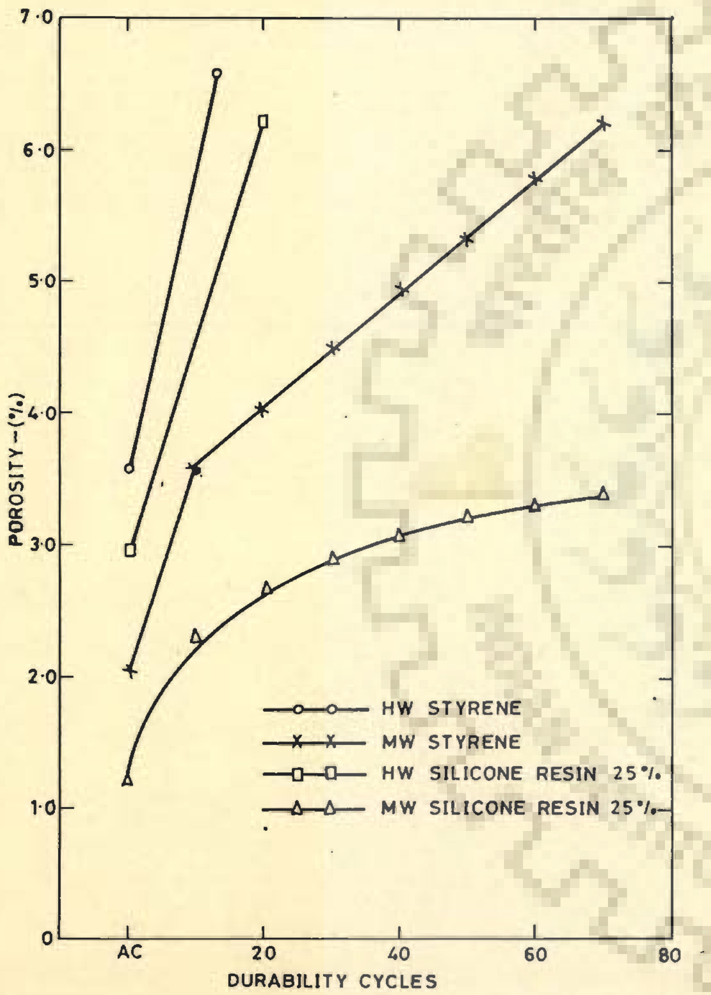


FIG6·2. VARIATION OF POROSITY OF TREATED BASALT WITH DURABILITY CYCLES

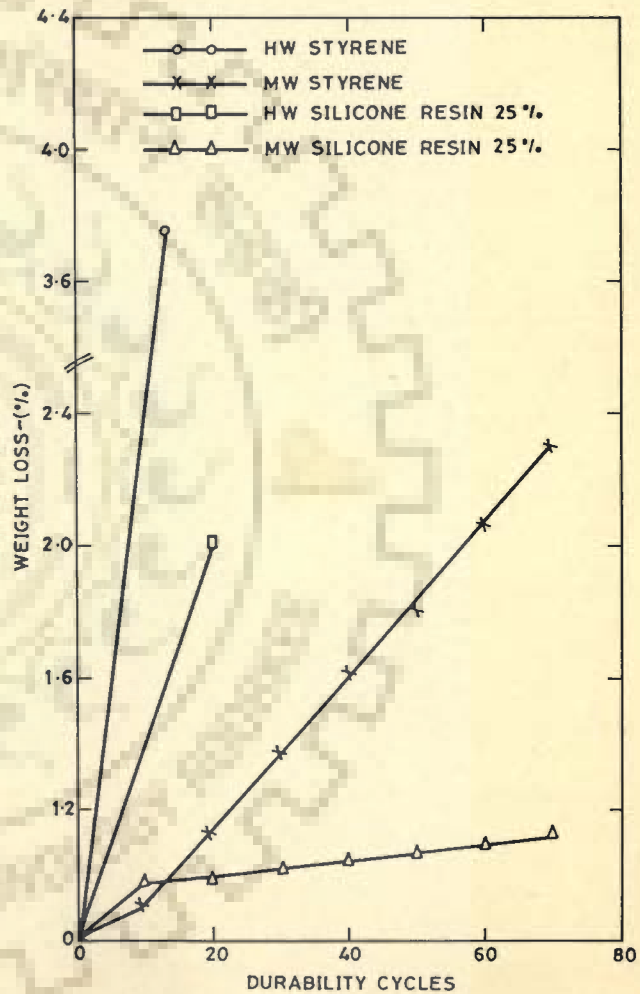


FIG.6·3. VARIATION OF WEIGHT LOSS OF TREATED BASALT WITH DURABILITY CYCLES

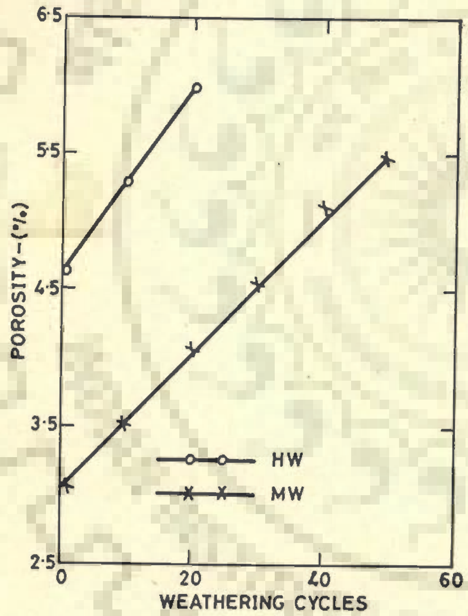


FIG.6·4. VARIATION OF POROSITY OF BASALT WITH WEATHERING CYCLES

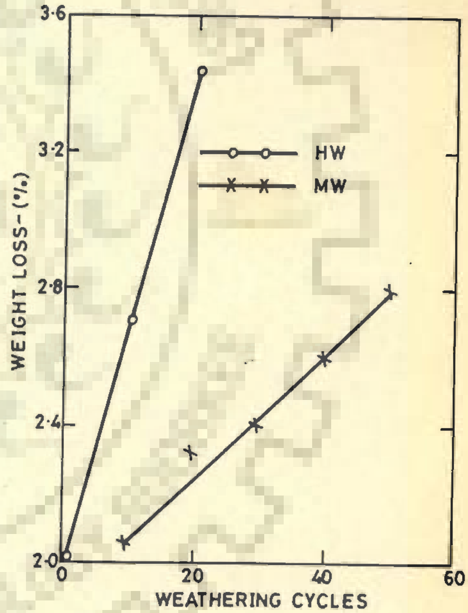


FIG.6·5. VARIATION OF WEIGHT LOSS OF BASALT WITH WEATHERING CYCLES

The extent of disintegration was very mild in comparison of durability tests(Fig. 6.5). The physical characteristics of the stone at the point of failure too confirm to great extent the findings of durability test results.

The untreated samples under sea water test show the progressive increase of porosity and weight loss. The treated samples under sea water tests have shown the efficacy of the preservative in marine environment. The HW basalt samples were found to sustain 10 test cycles when treated with styrene and 17 test cycles when treated with silicone based resin. Similarly the MW samples were found to be more resistant and did not fail after 50 test cycles when treated with preservatives. (Fig. 6.6 and 6.7). Fig. 6.8 shows the increase of weight loss of basalt samples with the concentration of sulphuric acid solution.

6.5 CONCLUSION

1. The study clearly indicated that the samples were already more or less in decaying stage. The highly weathered samples (HW) failed only in few test cycles under all the test, however, the moderately weathered samples (MW) failed after some more cycles.

2. Both HW and MW basalt samples got disintegrated after attaining certain fixed water absorption and porosity values. The WA values range from 2.0 to 2.5 percent and porosity from 6.1 to 6.8 percent.

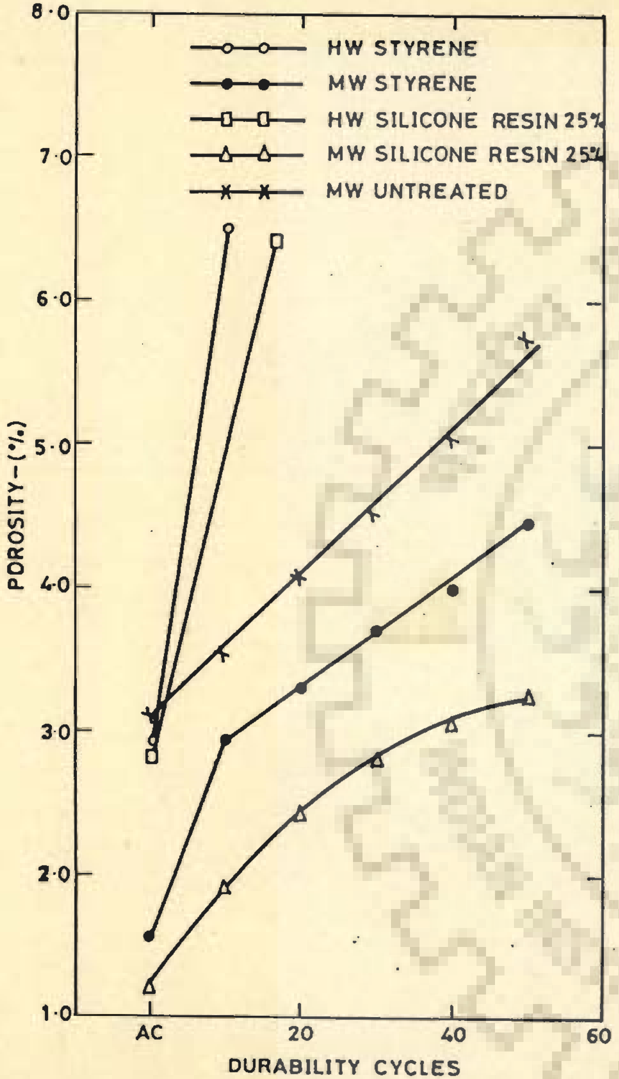


FIG.6·6. VARIATION OF POROSITY OF BASALT WITH DURABILITY CYCLES IN SEA WATER SOLUTION

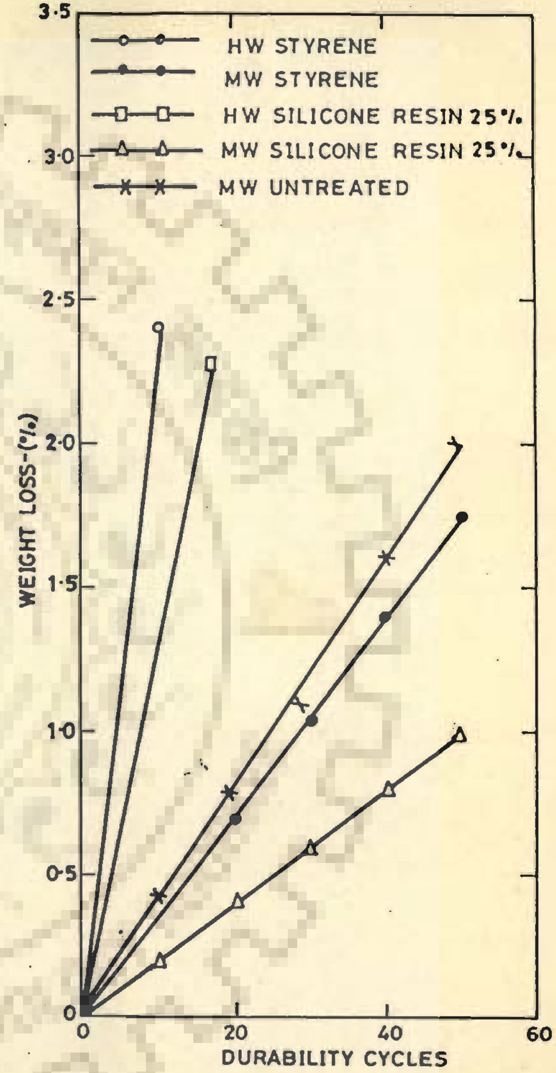


FIG.6·7. VARIATION OF WEIGHT LOSS OF BASALT WITH DURABILITY CYCLES IN SEA WATER SOLUTION

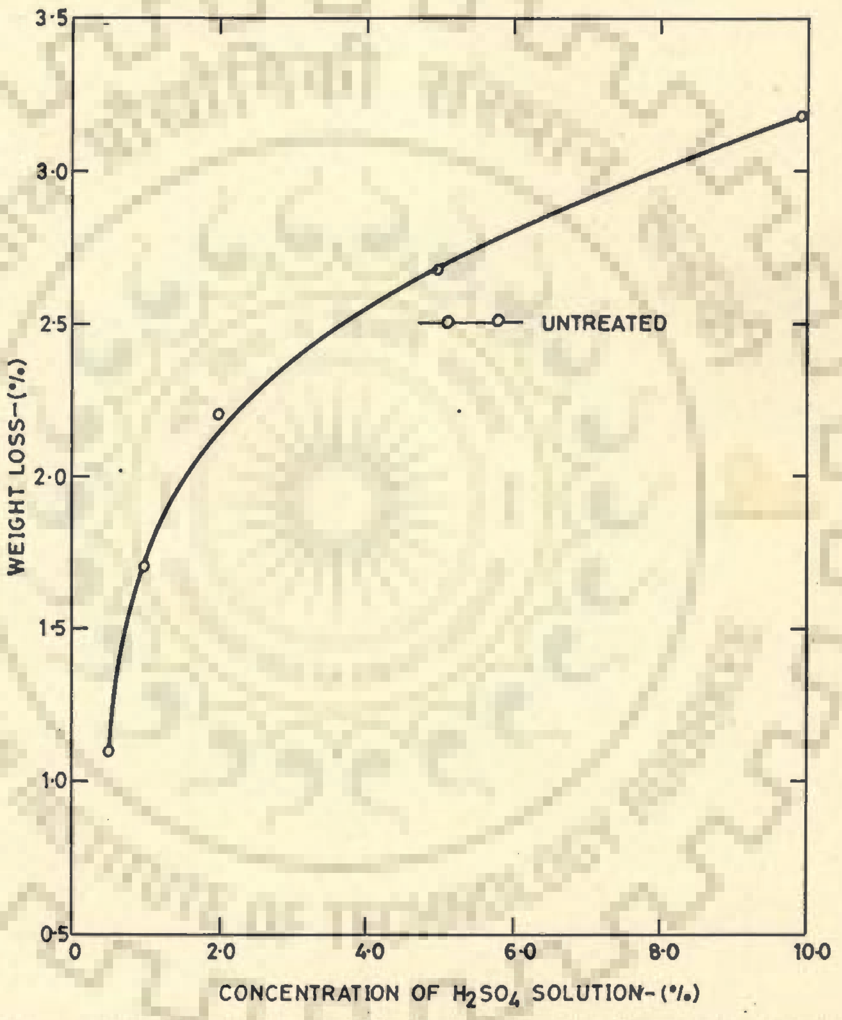


FIG.6·8. VARIATION OF WEIGHT LOSS OF BASALT WITH CONCENTRATION OF SULPHURIC ACID SOLUTION

3. The decay of basalt occurs mainly due to leaching of altered material filled up in the cavities of the stone forming grooves and pits over the surface. Development of crack, surface erosion and corner disintegration also occur in all the durability tests.

4. Among the preservatives, silicone resin was found to be the best for the conservation of this stone in the marine and salt environment.

CHAPTER VII

PHYSICO-CHEMICAL AND DURABILITY STUDIES OF SCORIA

CHAPTER VII

PHYSICO - CHEMICAL AND DURABILITY STUDIES OF SCORIA

7.1 INTRODUCTION

Scoria is a volcanic rock formed by the rapid cooling of lava. The rapid escape of gases from the lava results into the formation of cavities, bubbles or vesicles. The vesicles are numerous, often quite large and generally irregular in shape.

The scoria stone samples were collected from the Ramappa temple, situated in Hyderabad. This stone has been used at the top of the temple which is in the stage of deterioration. The collected scoria samples show variation in colour. The brown samples appear more softer than black samples. The present chapter describes the physico-chemical, mineralogical characteristics and durability behaviour of the stone under different simulated environmental conditions. The suitability of different preservatives namely silicone resin (25%) and PMMA (15%) for the preservation of this stone were also studied under the same tests.

7.2 EXPERIMENTAL PROCEDURES

Scoria samples were subjected to different physico-chemical, weathering and durability tests. The details of the procedures followed have been described in Chapter II.

7.3 RESULTS

7.3.1 Physico-Chemical Characteristics

The physical characteristics like water absorption, porosity, density, specific gravity etc. of scoria samples are given in Table 7.1. The samples show much variation in water absorption and porosity values. These values vary from 11.7 to 42.0 and 12.3 to 41.4 percent respectively. Generally the brown samples were found to have slightly higher values of water absorption and porosity as compared to black ones, however, no specific limit of these values between brown and blackish samples could be ascertained. The average values of true and apparent specific gravity were found to be 2.63 and 1.03 respectively. The bulk density and real density were obtained as 1.03 and 1.91 gm/cm^3 respectively. However, a large number of samples also showed the density below 1.0 gm/cm^3 as they float over the surface of water. The hardness of stone was found to be 1-2 (Mohr's Scale). The compressive strength of the stone varied from 6-15 kg/cm^2 depending upon their porosity and density.

Table 7.2 shows the chemical analysis of scoria samples of both brown and black colour. The results indicate that both samples have almost the same chemical composition showing siliceous and aluminous nature.

Table 7.1

Physical Characteristics of Scoria

Physical Characteristics	Average Experimental Value
Water Absorption(% by weight)	11.7-42.0
Porosity (% by volume)	12.3-41.4
True Specific Gravity	2.63
Apparent Specific Gravity	1.03
Real Density (gm/cm^3)	1.91
Bulk Density (gm/cm^3)	1.03
Compressive Strength (Kg/cm^2)	6-15
Hardness	1-2

Table 7.2

Chemical Analysis of Scoria

	Loss of Ignition (LOI) (%)	Silica (SiO_2) (%)	Iron Oxide (Fe_2O_3) (%)	Aluminium Oxide (Al_2O_3) (%)	Calcium Oxide (CaO) (%)	Magnesium Oxide (MgO) (%)
Brown sample	2.04	60.07	6.85	22.90	6.24	Nil
Black Sample	1.41	58.78	7.95	23.86	6.38	Nil

7.3.2 Mineralogical Analysis

The mineralogical studies carried out under microscope have shown that the main mineral in both the variaties of the samples are more or less same. It consists mainly of high temperature minerals cristabolite and tridymite varieties of quartz associated with volcanic ash and glassy phase constituents. The accessory constituents commonly ferrugenous constituents, however, show little variation in their quantities in the nature of distribution (Plate 7.1).

7.3.3 Weathering Test

The initial average values of water absorption and porosity of scoria samples were found to be 33.8 and 34.8 percent respectively. After 100 cycles of weathering test these values decrease to 10.8 and 10.5 percent respectively. The weight loss value after 100 cycles of test was found to be 4.94 per cent (Table 7.3).

7.3.4 Durability Test

Durability behaviour of untreated samples under two different conditions (No. 1 and 3, Table 2.2) are given in Table 7.4 and 7.5. The water absorption and porosity values of samples have been found to decrease progressively with respect to their initial values. The weight loss values, however, were found to increase in both the conditions. After 30 cycles of durability test these values were found to be 15.9 percent (test condition 1) and 2.29 percent (test condition 3).

Photomicrographs showing Scoria stone before and after the durability test:

Plate (7.1) Fresh Scoria sample showing the presence of high temperature minerals embedded in micro-crystalline to crypto-crystalline ground mass consisting of glassy or volcanic ash and carbonaceous matter (X100)

Plate (7.2) Scoria sample showing considerable loss of volcanic ash and carbonaceous matter making the ground mass enriched in high temperature forms of quartz grains (X100)

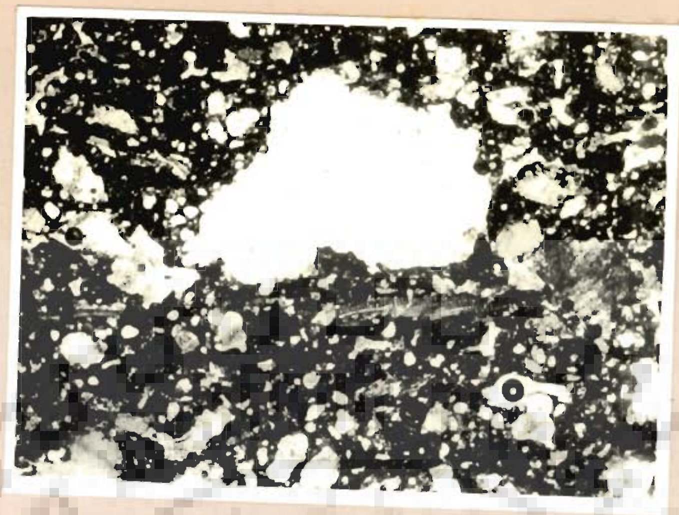


Plate 7.1: Scoria Stone
Before Durability Test x100

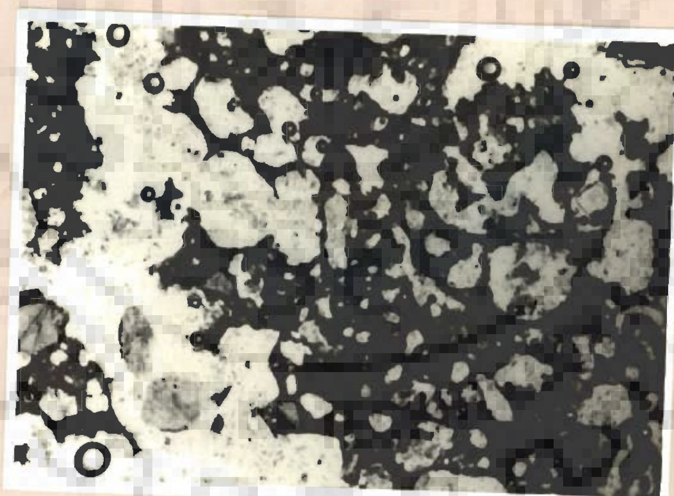


Plate 7.2: Scoria Stone after
Durability Test x100

Table 7.3

Variation in Physical Characteristics of Scoria Under Weathering Test

Initial		No. of cycles	Final		Weight loss
Water Absorption (%)	Porosity (%)		Water Absorption (%)	Porosity (%)	(%)
36.6	35.4	20	24.8	23.6	1.33
32.2	34.0	30	23.2	24.6	1.33
29.4	34.3	40	13.3	9.75	1.34
30.4	36.3	50	20.9	25.3	1.50
28.9	32.2	60	16.1	18.1	1.84
36.5	34.6	70	16.9	15.5	2.07
28.7	33.4	80	18.4	20.0	2.23
32.5	32.7	90	20.2	22.2	3.74
31.6	31.2	100	10.8	10.5	4.94

Table 7.4

Variation in Physical Characteristics of Untreated Scoria Under Durability Test Condition No.1

Initial		No. of cycles	Final		Weight loss
Water Absorption (%)	Porosity (%)		Water Absorption (%)	Porosity (%)	(%)
30.0	29.5	5	22.6	18.8	3.53
42.0	41.4	10	23.5	20.9	8.74
17.6	19.7	15	15.4	16.2	10.8
15.8	15.1	20	14.7	14.1	12.8
11.7	13.3	30	11.0	11.9	15.9

Table 7.5

Variation in Physical Characteristics of Untreated Scoria Under Durability Test Condition No.3

Initial		No. of Cycles	Final		Weight loss
Water Absorption (%)	Porosity (%)		Water Absorption (%)	Porosity (%)	(%)
16.3	12.3	10	16.0	12.7	1.12
18.1	15.9	20	15.2	13.2	1.19
26.2	23.1	30	24.7	21.0	1.50
23.3	21.0	40	20.6	21.1	1.70
31.5	25.2	50	26.8	20.8	2.00
22.8	23.3	60	22.2	22.7	2.10
17.4	17.1	70	14.2	13.7	2.29

Durability tests of scoria samples treated with silicone resin and PMMA under vacuum were carried out as per test condition 3. Test results are shown in Table 7.6. It shows that the treatment with silicone resin (25 percent), under vacuum, resulted into the decrease of water absorption and porosity values from 23.9 to 1.08 and 21.0 to 1.02 percent respectively. These values increased progressively under durability test and after 100 cycles of the test there were found to be 2.02 and 1.54 percent respectively without showing any significant sign of disintegration or surface deterioration (Plate 7.3).

Scoria samples treated with PMMA (15 percent) under vacuum have shown the decrease of water absorption and porosity values from 23.9 to 2.86 and 22.3 to 3.35 percent respectively. After 100 cycles of durability test these values increased to 7.90 and 9.16 percent respectively. Although no significant weight loss was found even after 100 cycles (Table 7.6 and Plate 7.4).

7.3.5 Sea Water Test

Table 7.7 shows the variation in water absorption, porosity and weight loss values of untreated and treated scoria samples under sea-water test. The results obtained showed the decrease of water absorption values for untreated stone from 23.2 to 14.9 percent and porosity values from 24.9 to 16.7 percent after 50 cycles. Weight loss was found to be 1.34 percent after 50 cycles.

Table 7.6

Variation in Physical Properties of Treated Scoria Under Durability Test

Treatment	Silicone Resin (25%)	PMMA (15%)	Silicone Resin (25%)	PMMA (15%)	Silicone Resin (25%)	PMMA (15%)
No. of cycles	Water Absorption(%)		Porosity (%)		Weight loss (%)	
Initial	23.9	23.9	21.0	22.3	-	
After coating	1.08	2.86	1.02	3.35	-	
10	1.10	2.95	1.03	3.61	0.226	Insignificant
20	1.18	3.19	1.09	3.76	0.229	''
30	2.25	3.98	1.15	4.80	0.249	''
40	1.40	4.58	1.21	5.19	0.270	''
50	1.50	5.23	1.27	6.11	0.300	''
60	1.55	5.29	1.30	6.66	0.320	''
70	1.71	6.60	1.46	7.37	0.352	''
80	1.80	6.80	1.50	8.00	0.400	''
90	1.86	7.40	1.52	8.55	0.448	''
100	2.02	7.90	1.54	9.16	0.479	''

Table 7.7

Variation in Physical Properties of Scoria Under Sea Water Test

Treatment / No. of cycles	Untreated	Silicone Resin (25%)	PMMA (15%)	Untreated	Silicone Resin (25%)	PMMA (15%)	Untreated	Silicone Resin (25%)	PMMA (15%)
	Water Absorption (%)			Porosity			Weight loss (%)		
Initial	23.2	22.9	20.1	24.9	19.8	20.2	-	-	-
After coating	-	1.22	2.86	-	1.28	3.33	-	-	-
10	21.8	1.22	3.00	23.2	1.02	2.09	0.519	0.11	Insignificant
20	20.1	1.26	3.10	21.7	1.35	2.60	0.959	0.19	''
30	18.0	1.42	3.21	Float	1.49	3.43	1.15	0.25	''
40	16.2	1.69	3.31	18.8	1.91	3.65	1.30	0.29	''
50	14.9	2.03	3.56	16.7	2.25	4.14	1.34	0.35	''

Plate 7.3: Scoria Treated with Silicone Resin under vacuum (100 cycles)

Plate 7.4: Scoria Treated with PMMA under vacuum (100 cycles)

Samples treated with PMMA showed increase of water absorption value from 2.86 to 3.56 percent and porosity value from 3.33 to 4.14 percent after 50 cycles, however, the samples didn't show any significant weight loss.

Samples treated with silicone resin showed the increase of water absorption value from 1.22 to 2.03 percent and porosity value from 1.28 to 2.25 percent after 50 cycles whereas the weight loss was found only 0.35 percent.

7.3.6 Acid Test

The effect of different concentration of H_2SO_4 on untreated as well as treated samples (Table 7.8) showed variation in weight loss from 2.29 to 3.77 percent for untreated samples, PMMA treated samples showed 2.19 to 7.58 percent variation, whereas with silicone resin these values varied only from 1.51 to 2.51 per cent with 0.5 to 10.0 per cent concentration of acid solution.

7.4 DISCUSSION

Scoria has been found to be very porous in nature. Due to variation in porous nature the samples show great variation in water absorption and porosity values. Generally the water absorption and porosity values of brown samples were found to be slightly higher than black ones, as the porosity values of brown samples were found to vary from 17.5 to 41.4 percent as compared to 12.3 to 34.1 percent for black samples. This could be due to the presence of more volcanic ash material. However, majority of samples of both colour have been found to have more or less same physical values indicating the same conditions of

Table 7.8

Behaviour of Scoria Under Acid Test

Treatment	Concentration of H_2SO_4 solution (% V/V) 0.5	1.0	2.0	5.0	10.0
	Weight loss (%)				
Untreated	2.29	2.42	2.50	3.10	3.77
S.R.(25%)	1.51	1.71	1.80	1.96	2.51
PMMA (15%)	2.19	3.29	4.96	7.40	7.58

their formation.

After subjecting to different tests, disintegration of samples was appeared in the form of surface roughness and corner disintegration and no cracking was observed. The disintegration pattern of stone under durability test is depicted in plates 7.5-7.7. The surface roughness resulted into a considerable weight loss of the samples. Weathering test resulted into 4.94 percent weight loss after 100 cycles of test (Fig.7.1). Durability test condition (1) resulted into maximum weight loss of 15.9 percent after 30 cycles, whereas test condition (3) resulted only 2.29 percent weight loss after 70 cycles of the test (Fig. 7.2). The samples under test condition (3) didn't show any considerable change in the appearance whereas the samples subjected to test condition (1) showed surface erosion, corner disintegration and reduction in size which increased with the number of durability test cycles indicating the aggresiveness of test condition (1).

It is interesting to note that the untreated scoria stone showed different behaviour and trend of decay than other stones in all the tests regarding the variation in its water absorption and porosity characteristics. After weathering, durability and sea-water tests the water-absorption and porosity values of untreated samples were found to have decreased with their respective initial values while the treated samples showed progressive increase. The decrease of these values for untreated stone could be due to the deposition of salt solution in the pores of the stone. The stone has large and more number of

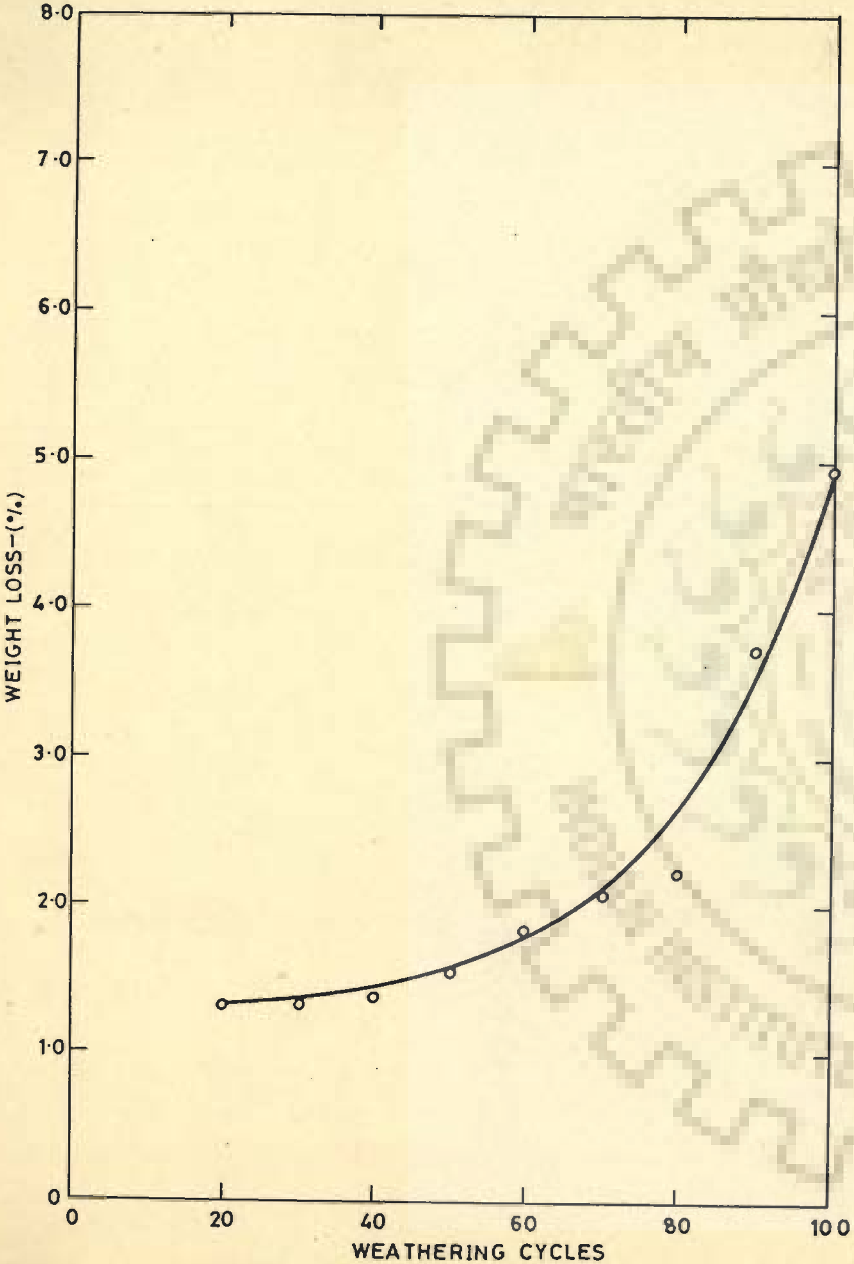


FIG. 7·1. VARIATION OF WEIGHT LOSS OF SCORIA WITH WEATHERING CYCLES

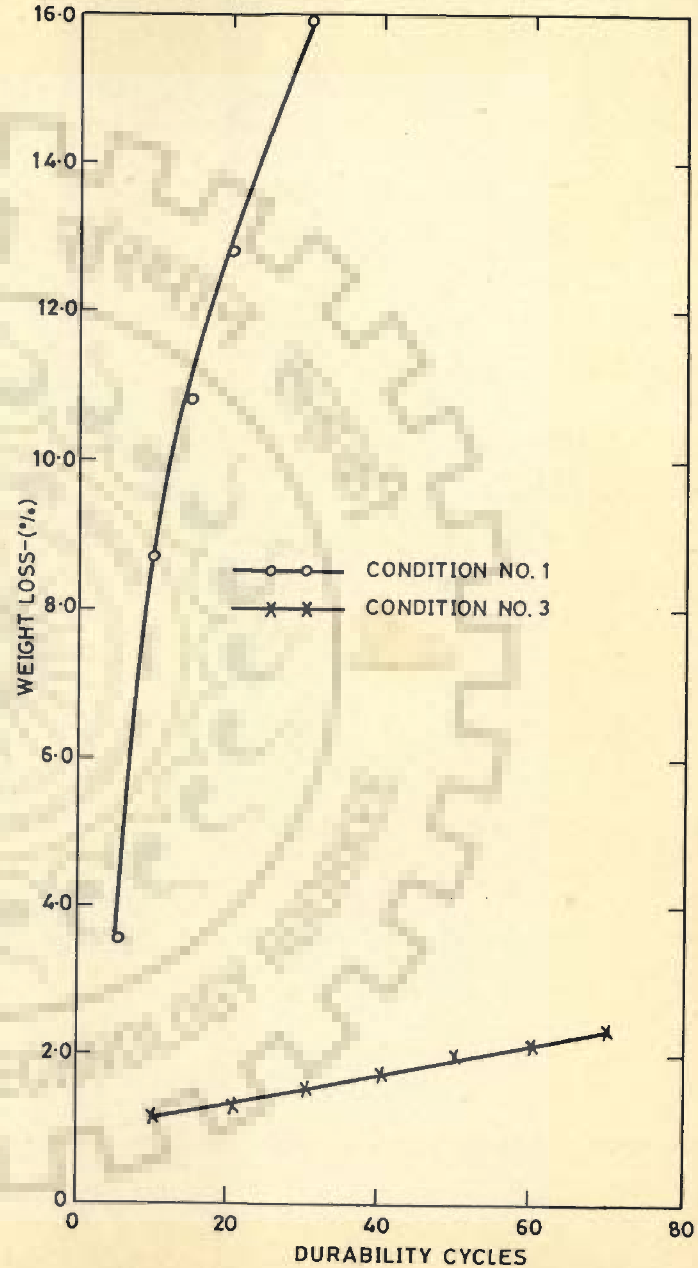


FIG. 7·2. VARIATION OF WEIGHT LOSS OF SCORIA WITH DURABILITY CYCLES UNDER DIFFERENT CONDITIONS

Plate 7.5: Untreated Scoria after 10 cycles of Durability test

Plate 7.6: Untreated Scoria after 20 cycles of Durability Test

Plate 7.7: Untreated Scoria after 30 cycles of Durability Test

pores so that all salt solution deposited and crystallised within the pores was not sufficient to cause disintegration effect on the pore walls of the stone.

The stone treated with both preservatives showed progressive increase of water absorption and porosity values under durability (Fig. 7.3) as well as in sea water test (Fig. 7.4). The rate of increase of these characteristics remained quite slow. The samples could not attain the original values even after 100 cycles under durability test. The decay in stone, however, can be assigned mainly due to repeated crystallisation of sodium sulphate in the pores causing removal of filled up preservatives. However, the samples treated with both preservatives show little or no weight loss during the tests indicating thereby the role of preservatives to improve the durability of stone (Fig. 7.5).

The concentration of H_2SO_4 solution was found to effect the durability of untreated and treated stones in terms of weight loss. The samples treated with PMMA have shown maximum loss in weight. More loss in treated stone than untreated indicate the ineffectiveness of the preservative in acid environment. The samples treated with silicone resin showed decrease in the rate of decay (Fig. 7.6).

7.5 CONCLUSION

1. The present chapter has clearly shown the trend of decay of scoria samples which has been found to depend on the development of pores of varying sizes and depths.

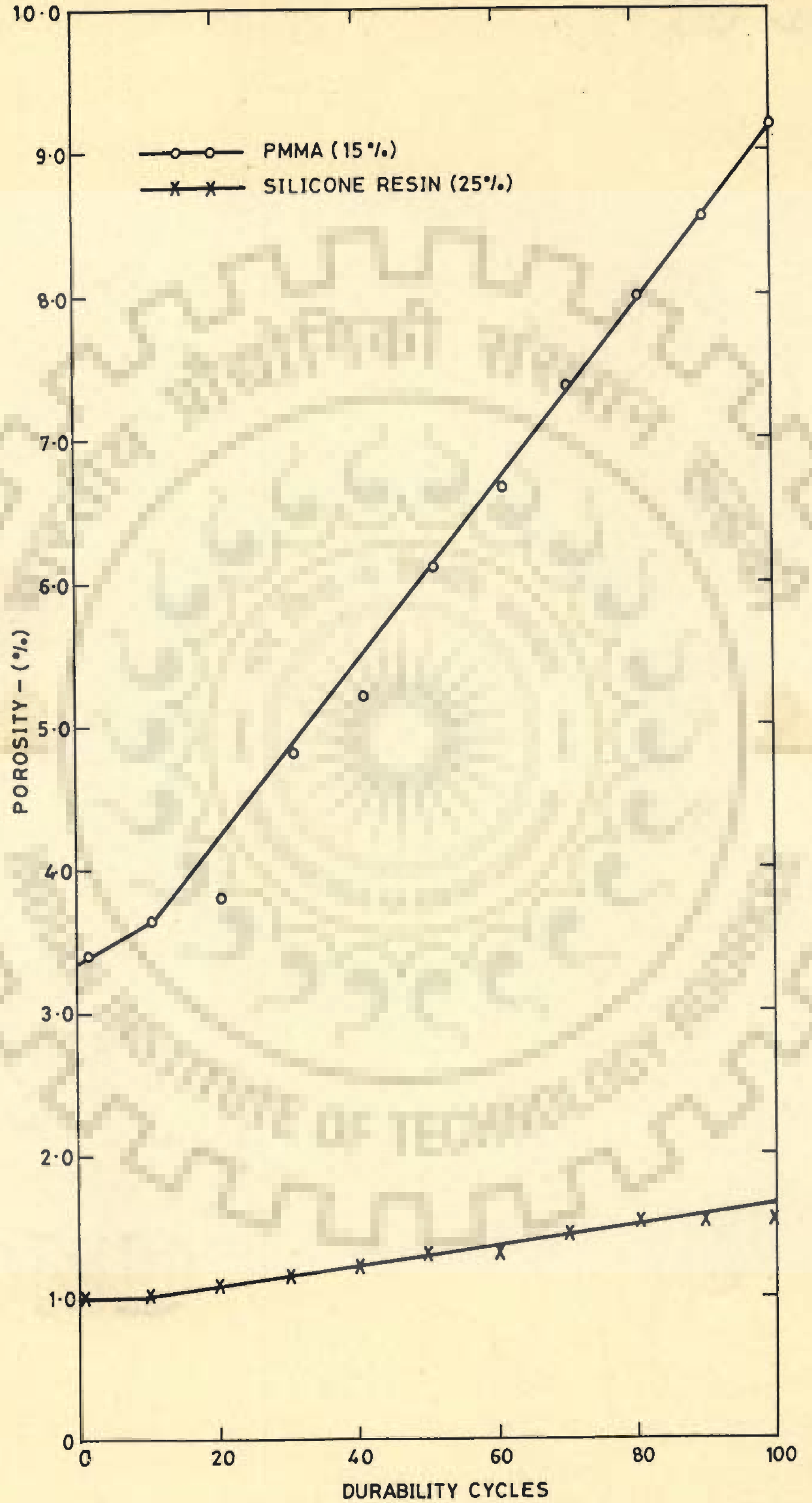


FIG.7·3. VARIATION OF POROSITY OF TREATED SCORIA WITH DURABILITY CYCLES

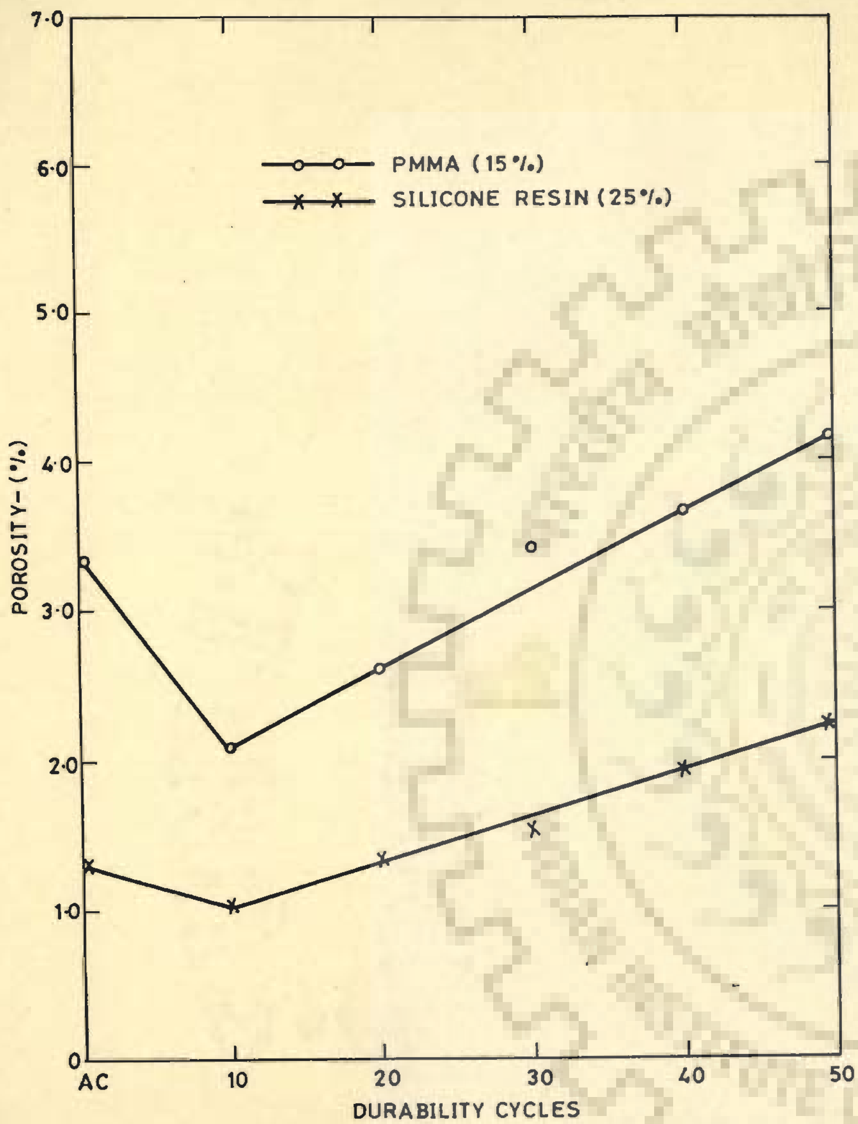


FIG.7·4. VARIATION OF POROSITY OF TREATED SCORIA WITH DURABILITY CYCLES IN SEA WATER

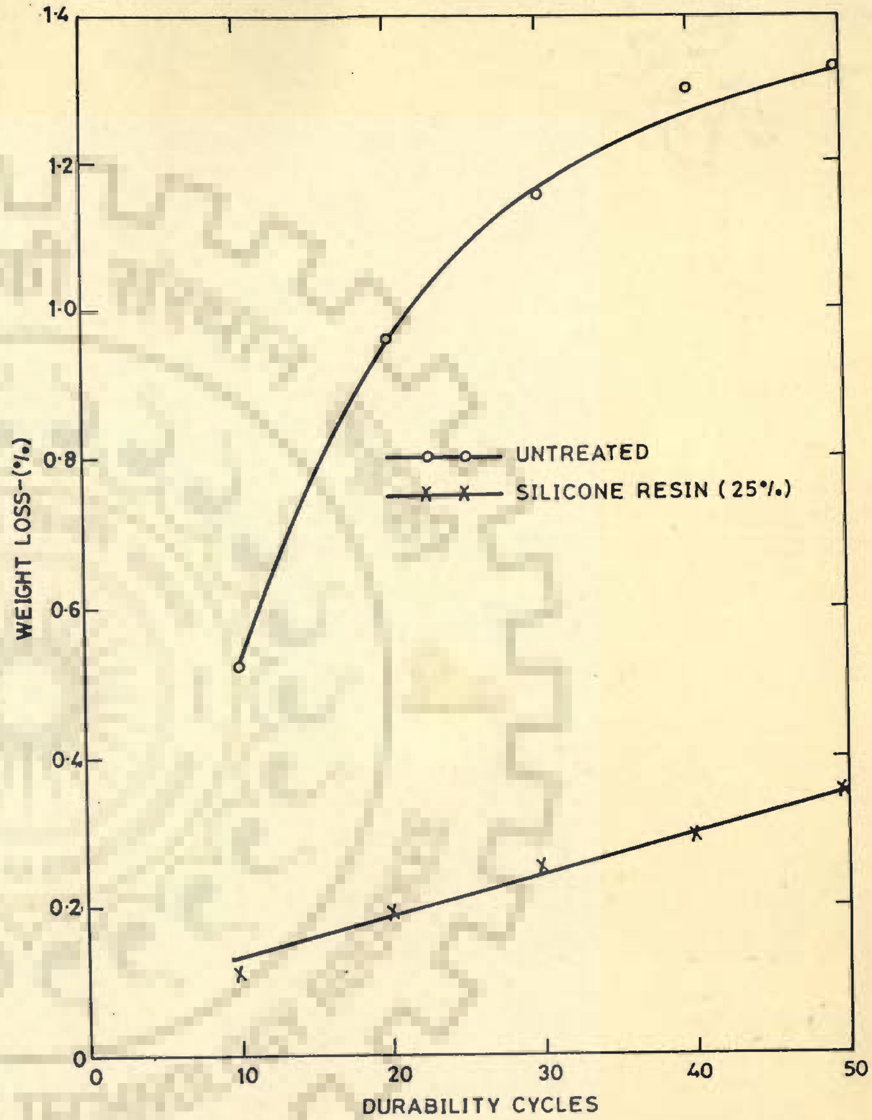


FIG.7·5. VARIATION OF WEIGHT LOSS OF SCORIA WITH DURABILITY CYCLES IN SEA WATER

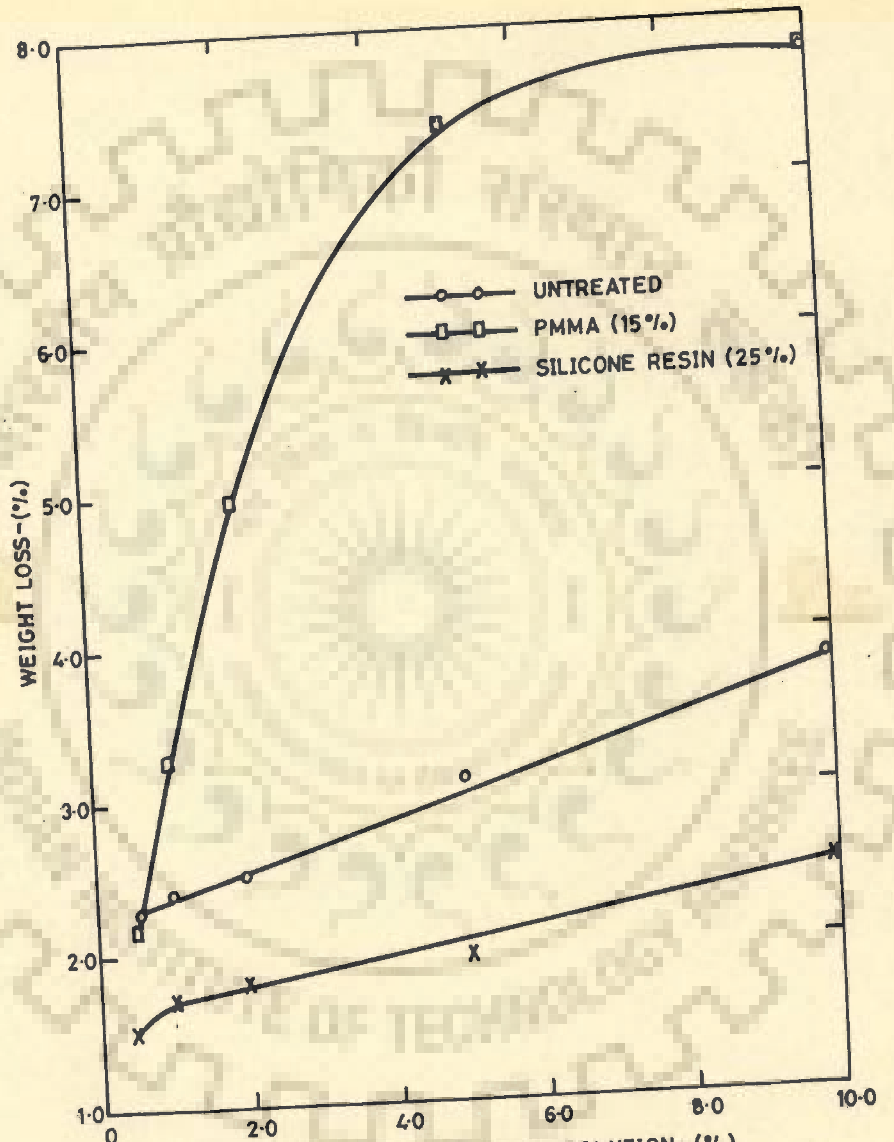


FIG.7·6. VARIATION OF WEIGHT LOSS OF SCORIA WITH CONCENTRATION OF SULPHURIC ACID SOLUTION

2. The decaying behaviour has been found to be different than the normal trend of other stones which has been explained due to repetitive deposition and crystallisation of salt solution in macro and micro pores.

3. The durability of scoria increases with the application of preservatives. Among preservatives, silicone resin has been found to more effective than PMMA in all the test.

CHAPTER VIII

SUMMARY AND CONCLUSION

CHAPTER VIII

SUMMARY AND CONCLUSION

The present study embodies the physico-chemical, mineralogical, weathering and durability behaviour of Makrana marble, red sandstone, white spotted sandstone, basalt and scoria, which have been commonly used for the construction of historical monuments of India. Samples of Makrana marble and both variety of sandstones were freshly obtained from their respective quarries, whereas, the samples of basalt and scoria were collected from the Elephanta caves and from Rammappa temple. The effectiveness of different preservatives were assessed for these building stones by examining their physico-chemical and durability behaviour before and after the treatments and also at various intervals of durability tests under different simulated environmental conditions. The present investigation also includes the identification and characteristics of microbial growth commonly found over the stone surfaces and their role in various modes of decay and deterioration of the stones.

The biological studies clearly indicated the wide adaptibility of microbial-growth towards the stone monuments built with Makrana marble, sandstones, and even on mortar material. The results showed the common occurence of Cyanophyceae algae and bryophytes growth over the stone surfaces.

Cyanophyceae algae have been found to be commonly present in all the sites examined. The possible reason for the wide presence of Cyanophyceae algae could be assigned to the presence of accessory pigments (phycobilin) which allow them to survive in low light conditions. Altogether 17 species of Cyanophyceae could be identified, among which, two members were found to be substrate (calcareous) specific in nature. Cyanophyceae algae have the degrading effect on stones by the secretion of organic acids and also work as a ground for the development of other microbes. Among bryophytes, Riccia and funaria were abundantly found, having always a dried blackish layer of algae and other humus deposition beneath it. The presence of moss further permits to develop higher plants. Thus the development of microbial population over the stone surfaces can cause morphological, mechanical and chemical changes in the stones, which further enhances the decay of stones.

During the course of survey of the monuments it has been observed that the microbial growth occur on rough, cracked or disintegrated stone surfaces. On smooth surfaces their presence in insignificant. This shows that besides the availability of general requirements for their development, the growth starts with the disintegration of stones. Thus the implementation of preservative found suitable to enhance the durability of the stones can also be considered to retard the microbial growth over the surfaces. The experiments carried out have proved this inference.

The physico-chemical studies on each variety of stone have clearly revealed the general trends of decay of stones. The decaying behaviour of stone has been found to have direct relation with the inherent physical characteristics e.g. water absorption and porosity, texture and structure of the stone. The general trend found commonly in most of the cases is the progressive increase of water absorption and porosity with the decay of stone.

A significant and important feature emerged from this study is that the stone get deteriorated when it attains certain fixed values of water absorption and porosity. In case of Makrana marble it has been observed that it disintegrates when the water absorption and porosity values become around 0.25 and 0.720 percent respectively. In the case of red sandstone the average values of water absorption and porosity at the disintegration stage have been found to be 3.94 and 10.3 percent respectively, whereas, for white spotted sandstones these values are 3.14 and 7.25 percent respectively. The basalt samples examined have shown that both highly weathered (HW) and/moderately weathered (MW) samples failed having 2.0-2.5 percent water absorption and 6.0-7.0 percent porosity values.

Based on the relationship established between the physical characteristics and decaying behaviour of stone by this study one can easily assess the present state and remaining life of the similar stone used in the monument in any part of India. And, thus the decision for the implementation of the preservative for the conservation of stone monument can be taken well in advance.

A comparative study of the durability behaviour of stones under different test conditions has clearly exhibited the effect of different parameters of durability test e.g. concentration of salt solution, immersion time, drying time and temperature. The results showed that the variation in immersion time having same concentration of solution and drying temperature does not cause any significant effect in decaying behaviour of the stones. The physical properties e.g. water absorption, porosity and weight loss also remain more or less same. The change in drying temperature, however, has shown significant effect on durability behaviour e.g. the Makrana marble which failed around 32-40 cycles at 105°C drying temperature (test condition (1)) had understood 100 cycles at 60°C drying temperature (test condition (3)). Even after 100 cycles the water absorption and porosity values were found to be much lower than the values under test (1). Similar trends have been found in other varieties of the stones studied under the durability test.

The pattern of disintegration of stone has been found to be dependent on the texture and structure of the stones. In Makrana marble the disintegration starts with the surface roughness followed by corner distortion and resulting into the development of cracks in irregular fashion. The disintegration of sandstone has been found to begin with the loss of cementing material both from the surface as well as along the bedding plane. The cracks generally appear along the bedding plane which deepen with the decay of stone. The stone pieces finally get separated along the bedding planes. Some vertical cracks do appear in the advanced stage of decay. The decaying pattern of basalt starts with the leaching of the material forming amygdals resulting into the development of grooves and pits over the surface. Later, brownish (ferrugenous) material appears more on the surface. The degree of disintegration of basalt can easily be assessed on the basis of grooves, pits and presence of brownish (ferrugenous) material on the surface. In the final stage, the cracks appear and stone crumbles. The scoria samples showed the decaying pattern in the form of heavy surface erosion causing damages to the porous structure and corners of the stone resulting into the friability of stone.

The durability and weathering characteristics of scoria samples were found to be indifferent than other stones. The physical properties e.g. water absorption and porosity of untreated stone have been found to have decreased with the decaying cycles. To some extent this could be due to its typical origin and characteristic structure and texture. During the tests, possibly the salts get deposited within the large pores of stone causing reduction in the porosity.

For detailed investigation on the suitability of various preservatives namely barium hydroxide, polymethyl methacrylate, styrene and silicone resins were applied on stones under vacuum and by brushing technique. The preservatives have more penetration in stones under vacuum than brushing as the results showed that the samples treated by brush failed earlier than the samples treated under vacuum. The results further showed that the application of preservatives in general enhance the life of stones. Among the preservatives, tried in this study, the silicone resin has been found to be the most effective preservative under different environmental conditions. Silicone resin forms strong adhesion bonds with the stones and also preserves the original colour, structure and texture of the stones.

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