

doubling the collector concentration could complete recovery be achieved. This incipient collector concentration was deliberately chosen to study the effect of sonication on flotation recovery.

Flotability of galena in the presence of ultrasonication with Na-isopropyl xanthate is shown in Figure 1b. As is evident, ultrasonication improved the flotation recovery up to 30 minutes, but recovery decreased beyond this period due to the formation of excessive amounts of slime which consumed the available collector reducing the per cent floated material. This observation can be corroborated with the finding of Celik⁸. Ultrasonic pretreatment of the pulp activates the galena surface for collector adsorption.

Figure 2a shows the effectiveness of ultrasonication with stirring in distilled water followed by collector addition and conditioning. It was presumed that introduction of stirring in distilled water (no collector) during ultrasonication prevented adsorption of some collector by slimes. Subsequent addition of collector followed by conditioning (5 minutes) led to substantial improvement in recoveries. Exposure of the clean galena surfaces which are more conducive to xanthate adsorption resulted in

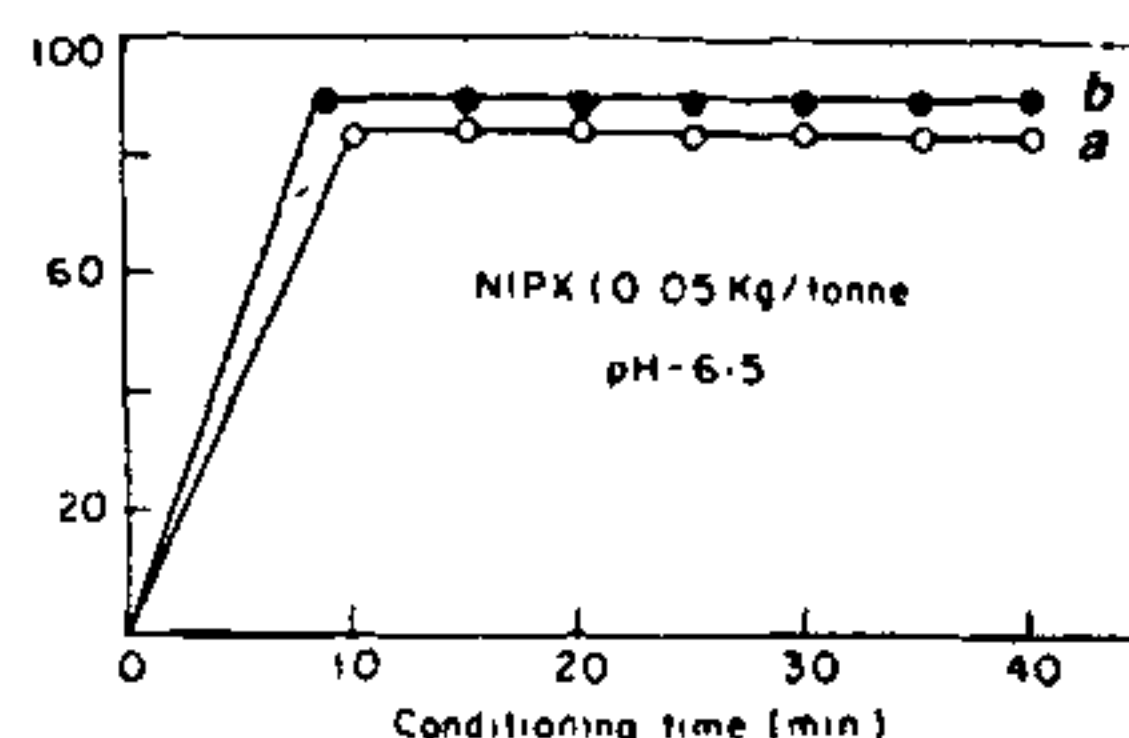


Figure 2. Effect of ultrasonication on the flotability of galena. *a*, sonication + stirring in distilled water + 10 min conditioning with collector; *b*, sonication + stirring in distilled water + 10 min conditioning with collector + desliming

higher recoveries, despite the presence of slimes.

Figure 2b corresponds to the conditions of Figure 2a except for the desliming prior to flotation. The flotation recovery in this case was found to be higher. The presence of slime generally hinders particle-bubble attachment and leads to excessive collector consumption. The above results indicate that ultrasonication under appropriate conditions can achieve at least a 40–50% reduction in collector consumption. The imposition of ultrasonication creates a surface which is not only partially hydrophobic but also highly conducive to collector adsorption.

1. Singh, B. P. and Singh, R., *J. Inst. Eng. (India)*, 1992, (C)
2. Sastri, V. S. and Mackinnon, J. *Sci. Ind. Res.*, 1977, 36, 379–385.
3. Celik, M. S. and Somasundaran, P., *Colloids. Surf.*, 1980, 1, 121–124.
4. Zubkov, A. A. and Belov, B. G., *Tsvtn. Metall.*, 1982, 9, 102–106.
5. Kowalski, W. and Kowalska, E., *Ultrasonics*, 1978, 16, 84–86.
6. Nicol, S. K., Engel, M. D., Tech, K. C., *Int. J. Miner. Process*, 1986, 17,
7. Slaczka, A. St., *Int. J. Miner. Process*, 1987, 20, 193–210.
8. Celik, M. S., *Sep. Sci. Tech.*, 1989, 24, 1159–1166.
9. Reunivtzev, V. I. and Dmitriev, Yu. G., *Proc. Seventh Int. Miner. Congress*, New York, 1964, pp. 43–49.
10. Manukonda, R. V. K., Ph.D. thesis, University of Minnesota, 1985, p. 200.
11. Eremin, Yu. P., *Chem. Abst.*, 1980, 93, 51296.
12. Singh, B. P. and Pandey, B. P., *Res. Ind.*, 1991, 36, 203–207.
13. Singh, B. P. and Pandey, B. P., *Proc. Indian Natl. Sci. Acad.*, 1992, 58A, 181.
14. Arol, A. I. and Iwasaki, I., *J. Miner Metall. Process*, 1987, 82–87.

Received 24 August 1992; revised accepted 7 December 1992

B. P. Singh is in Regional Research Laboratory, CSIR, Bhubaneswar 751 013, India

Studies on weathering of Kailasanatha Temple, Kancheepuram

M. Singh

Kancheepuram, situated about 65 km from Madras is a treasure trove of art and architecture as it houses more than 300 ancient temples. During the heydays of Pallavas, this city was a citadel of learning. Among the monuments of Kancheepuram, the Kailasanatha temple is the most important and was built by Raja Sinha Pallava in the 8th century AD. Vikramaditya, a second Chalukya ruler, though invaded Kancheepuram, he ordered preservation of the monument and its sculptures. It is also said that granite slabs were laid for conservation of the temple by Mahendra II.

The temple consists of the main Vimana (Figure 1) a four-storey structure, and was named after its builder Rajasimheswara. On the eastern side, there is a small shrine called Mahendravermeswara, built by his son Mahendra Varman. The entire temple complex is surrounded by a compound wall which was built in array of 58 cells (Figure 2) on the inner side and contains figures of Gods and paintings.

The temple was constructed with dark yellowish sandstone as well as granite which was a later addition. The sandstone particles are medium-to-fine

grained consisting of quartz cemented by calcite. The deterioration of the temple was due to biological growth and salt action. Salts were carried by speedy sea winds or capillary action. Due to this as well as the variation in atmospheric conditions, sandstone lost its compactness and became powdery. The surface was so pulverized that sharp features of the sculptures and fineness of the ornamental design were lost (Figure 3). The plinth walls and pillars of the cells lost their finely-chiselled polish surface and show sand particles loosely adhering to the surface.



Figure 1. A view of the Kailasanatha Temple, Kancheepuram.



Figure 2. The inner cells of the temple.

The Vimana became black due to biological growth.

The effects of salts on building stone have earlier been studied¹⁻⁴. Durability of the stone used in building was normally determined by the rock porous structure⁵. Salt crystallization can be disruptive or cementing depending on the pore structure of the stone and the crystallization pressure that develops within the pores⁶. Porosity also helps in distinguishing the state of weathering of a particular rock as compared to in-situ specimen. Studies on the distribution of soluble salts that cause alteration of sculptured stones show that they concentrate near the surface of the stone. This is because the pores near the surface of the stone have been filled with crystallization salts and the resulting high crystallization pressure may be responsible for exfoliation and crumbling

of the stone structure, leaving the stone surface more porous and prone to attack by various decay causing factors. Also the colloidal minerals acting as the cementing medium between silica grains allow easier movement of moisture in sandstones, hence drying takes place from the surface resulting in excessive crystallization of salts on the surface. There is a correlation between the flow of salt solution through the capillary system, the rate of evaporation and the effect of salt crystallization in stone⁷. High crystallization pressure is shown to be associated with stone structure where a substantial percentage of small pores are present.

The growth of cryptogamic plants and acid pollutants also corrode the minerals present in the rocks. Decay of vegetable matter on the stone surface results in a larger concentration of CO₂

and other weak organic acids in the weathering belt causing more damage. Sometimes thin crusts are formed on the stone over a period of time due to natural agencies, which are pleasing in appearance and are called patina. Since patina forms an integral part of the stone surface and adds to its aesthetic value, it should not be removed during chemical treatment.

Preservation of salt-laden monuments is a difficult task and an attempt has been made to discuss the factors involved and the conservation treatment that is needed. Since characterization of the type of stone influences the conservation treatment, a sound knowledge of stone structure and decay process is necessary to find out the best consolidants for each particular case. The conservation treatment can also be extended to a large number of similar sandstone structures at Kancheepuram which are not under the purview of the Archaeological Survey of India.

Experimental

The surface of Kailasanatha temple is exposed to the atmosphere and can be studied on the spot by direct observation and with aid of hand lens. For laboratory analysis, small samples from the surface of the monument were utilized. Comparison was made with a good sample available near the monument to assess the magnitude of decay that has taken place since the construction of the temple. Stone samples bearing numbers 1 to 6 represent the weathered sandstones collected from various parts of the monument and sample 7 represent sound, unweathered sandstone. Samples 8 and 9 represent weathered and unweathered granites respectively. All the samples were chemically analysed at the Geological Survey of India, Bangalore on a Varian-Tectron atomic absorption spectrophotometer by a process described elsewhere⁸. Petrological data of the samples were obtained from the Geological Survey of India, Hyderabad. SEM micrograph of the sample was carried out at the Archaeological Survey of India, Dehradun. Due to lack of instrumentation, only the apparent porosity of the samples was determined in the laboratory. The aqueous extract of the samples was measured using an ion



Figure 3. Loss of ornamental design due to weathering.

analyser (Orion, 407 A) at the Birla Institute of Scientific Research, Hyderabad. Loss on ignition (LOI) was determined at 900°C using a muffle furnace.

Observations

Microscopy

The materials under examination were soft and friable. The grain consisted of small angular particles of quartz with occasional biotite fragments. The size of most of the grains was uniform but the undecomposed stone was finer in

grain size than the weathered stones. The proportion of ferric oxide under microscope varied in different stones in roughly the same manner as that shown by chemical analysis, the unweathered stone showing the largest amount.

Petrology

Petrographic model analysis of seven sandstone samples and two granite samples of the monument is shown in Table 1. Mineralogically the rocks comprise of plagioclase, orthoclase, microcline, quartz, chlorite, chloritized biotite,

lithic fragments and calcite, the later as cementing material. Petrographic thin section of the rock shows that all the minerals are angular and exhibit poor sphericity and irregular shapes. The grains were not uniform and varied from 0.04 mm to 0.7 mm. However, the majority of the grains was in the range 0.3 to 0.5 mm.

The plagioclase feldspars altered to dusty turbid material (sericite and kaoline). The grains of samples 3 and 4, taken from cell numbers 39, 40 and 14, 15 respectively, were of similar size and angularity with little difference in the amount of plagioclase component. Quartz

Table 1. Petrographic model analysis of sand stones/granites of the temple

Mineral %	Sample numbers								
	1	2	3	4	5	6	7	8	9
Quartz	28.14	27.16	28.32	31.26	33.84	33.06	25.14	23.5	31.02
Calcitic minerals	23.36	24.82	24.57	23.93	24.83	22.48	27.22	—	—
Aluminium minerals	41.53	38.62	38.15	38.12	36.20	36.23	31.84	71.71	57.64
Iron minerals	2.08	3.36	3.56	2.4	2.08	2.72	8.8	0.74	4.64
Biotite and other lithic fragments	3.64	4.09	3.6	3.45	2.64	3.64	5.3	2.38	5.65
Total	98.75	98.05	98.2	99.16	99.59	98.13	98.3	99.38	98.93

grains show undulose extinction. Very rarely tiny inclusions of zircon and apatite were seen in the quartz, chlorite and biotite occurring as irregular flakes.

All the clasts were bounded by a carbonate and at places by ferruginous cement. The carbonate (admixed with kaoline) cement and clast ratio was 20%:80%. The rock was classified as feldspathic sandstone. X-ray diffraction pattern confirms the presence of kaoline as altered dusty material in the weathered rock. The ferromagnesium minerals such as biotite became chloritized and further broke down to various soluble and colloidal substances.

From Table 1 the mineralogical proportions of unweathered to weathered stone are noteworthy. The ferruginous cementing material of sandstone appreciably weathered resulting big changes in the other mineral constituents of the rock. Quartz grains liberated by weathering of feldspar have dull and corroded surface. Further alteration of the surface of the monument since its construction and consequent leaching and erosion by atmospheric action aggravated the deterioration of monument rock. Due to capillary action of groundwater, the samples examined from the plinth walls of the cells and pillars of Mandapa showed much weathering.

Chemical analysis

Chemical analysis of the weathered/unweathered samples of sandstones/granites showed a higher concentration of sodium and potassium salts on the weathered stones. This brought about considerable changes in the rock producing secondary and residual products quite different in lithological properties than the original rock. The result of chemical analysis is shown in Table 2.

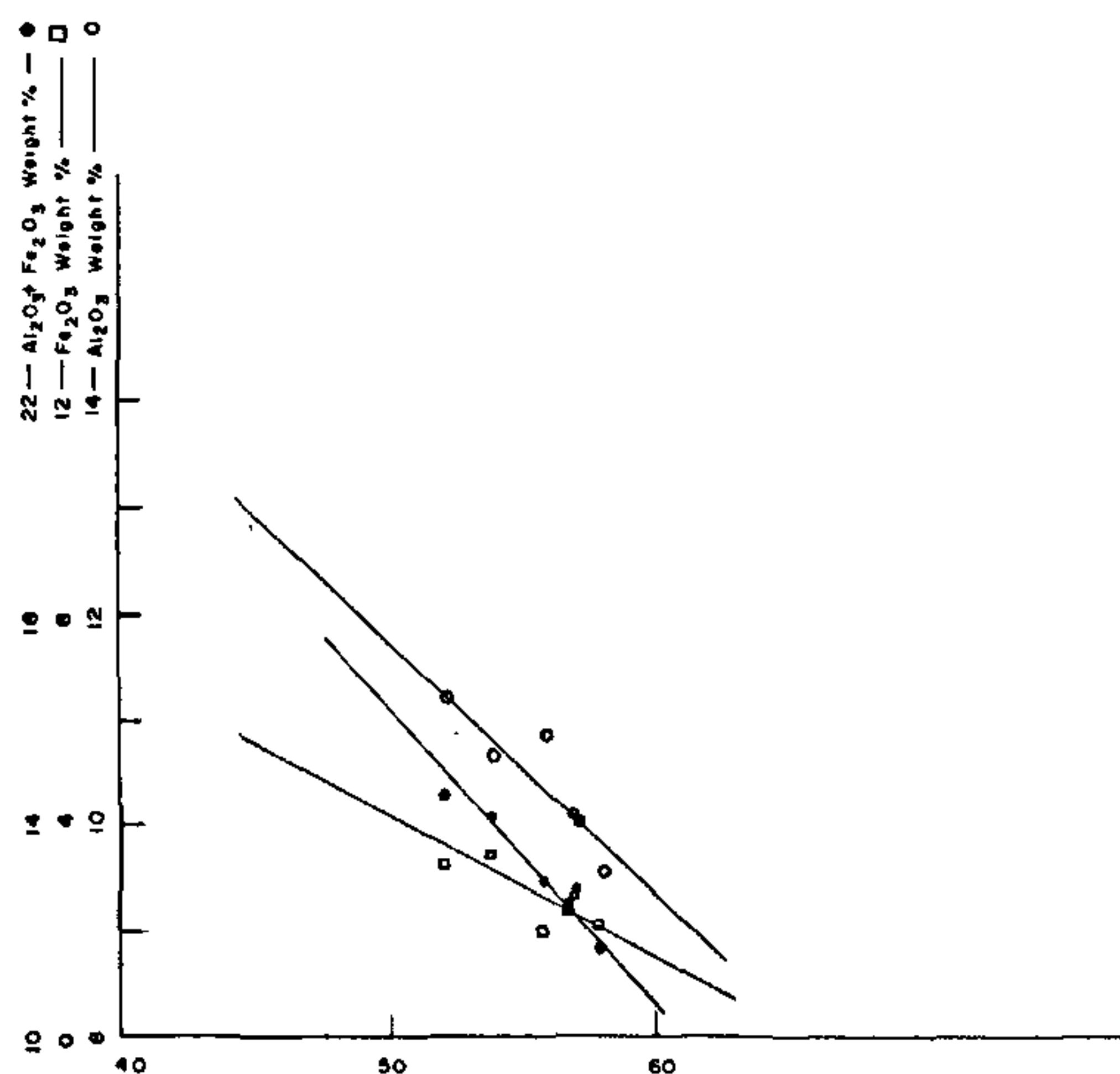
The relation between SiO_2 and Al_2O_3 or Fe_2O_3 in the sandstone samples is almost linear and complementary show-

ing that Al_2O_3 or Fe_2O_3 decreases with corresponding increase in SiO_2 (Figure 4). Al_2O_3 and Fe_2O_3 taken together show similar relationship with SiO_2 (Figure 4). In general, a decrease in Al_2O_3 is seen to register a much larger decrease in the Fe_2O_3 content. This

indicates that $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ together may be taken as an index of weathering. Analytical results also show a gradual increase of silica with corresponding increase in sodium and potassium oxides on the weathered stone. Hence, in conjugation with other factors of

Table 2. Chemical composition of sandstones/granites of the temple

Constituent (%)	Sample numbers								
	1	2	3	4	5	6	7	8	9
SiO_2	55.87	52.07	53.70	57.14	57.95	57.20	46.40	71.85	68.02
Fe_2O_3	2.06	3.35	3.51	2.45	2.13	2.75	8.74	0.74	4.60
Al_2O_3	10.92	11.28	10.73	10.15	9.60	10.12	13.17	14.41	14.68
TiO_2	0.18	0.32	0.36	0.29	0.25	0.27	0.40	0.12	0.20
CaO	12.36	12.80	12.51	12.35	13.11	11.66	13.53	1.28	1.28
MgO	0.62	0.96	1.10	0.93	0.70	0.80	1.45	0.20	1.23
Na_2O	2.47	2.72	1.95	2.50	2.05	1.99	1.87	4.89	4.17
K_2O	3.45	2.64	3.18	3.15	3.25	3.33	2.75	4.76	2.70
MnO	0.13	0.33	0.12	0.20	0.16	0.16	0.28	0.01	0.23
L.O.I	10.36	13.24	12.00	11.20	11.60	10.80	10.39	0.50	0.72
Total	98.42	99.71	99.15	100.36	100.8	99.08	98.93	98.76	99.10

Figure 4. Variation of SiO_2 with Al_2O_3 , Fe_2O_3 and $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$.

degradation of rocks, crystallization of soluble salts of sodium and potassium plays an important part in the weathering process of the rocks.

In the decomposition of rocks, important reactions are those which lead to destruction of feldspar. Slightly acidic water can react with many aluminosilicates to produce alkali and alkaline earths. The alkaline solutions thus formed become potent agents for further desilication. In the moist-tropical conditions prevailing at Kancheepuram, the decomposition goes further and the combined silica of feldspars and other silicates are completely removed, leaving a residue of hydrated oxides of iron, aluminium and manganese together with much of the quartz originally present in the rock. Thus the weathering of the monument stone is characterized by an abundance of quartz grains released by the destruction of less stable silicates. Quartz, zircon etc., are of longer grain size and remain on the surface while the other weathering products are washed down from the surface by various natural agencies. The increased silica on the rock surface may be regarded as natural skin or patina which may afford a certain degree of protection to the underlying stone. If this skin is damaged, the powdery under-surface is exposed. The weathering of monument rock is quite interesting and unique due to the above features.

Porosity determination

The presence of small pores (micropores) is a greater disadvantage than the presence of large pores (macropores) and hence the measurement of microporosity is more useful in assessing the quality of sandstone than the measurement of total porosity. Due to lack of instrumentation, this feature could not be confirmed and only the apparent porosity of the stone was determined. The test on sand-stone samples reveals that apparent porosity ranges from 3.24% to 5.2%. The chip prepared from surface specimen shows higher porosity (4.82%) while the chip prepared from inside the surface shows lower porosity. The undecomposed sample shows still lower porosity of 2.4%. These determinations reveal that the monument rocks have been rendered more porous especially at the surface. Leaching out of

weathered products contributed to increased porosity of the monument rock.

Aqueous extract

It is important to know the salts in the aqueous extract of stone materials because they contribute to the decay of the stone. Sea water with its relatively high ionic strength accelerates the solution process of the rocks. The aqueous extract of a fairly weathered sample of sandstone was determined (Table 3).

The results shown above are characterized by an increase in the total dissolved solids (TDS). The magnitude of such enrichment of TDS may only be due to salt deposited in the pores of the stones.

SEM micrographs of stone samples

In order to compare the structural alteration, both weathered and unweathered stones were scanned on a Hitachi-450 SEM. The SEM micrographs of weathered sand stones show the presence of quartz, feldspar, felsic minerals, loose quartz grains, calcite and biotite. The grain sizes are heterogeneous. Cracks and cavities filled with ferruginous cementing material can be very distinctly seen. The micro-morphology of unweathered rock is quite different. The grains of constituent minerals are quite intact, homogeneous and without any structural defects. Figures 5a-d illustrate the cross-section of decayed sandstones. Figures 5e, f show micrographs of a sound sand stone and granite stone respectively.

Table 3. Composition of aqueous extract of the sample

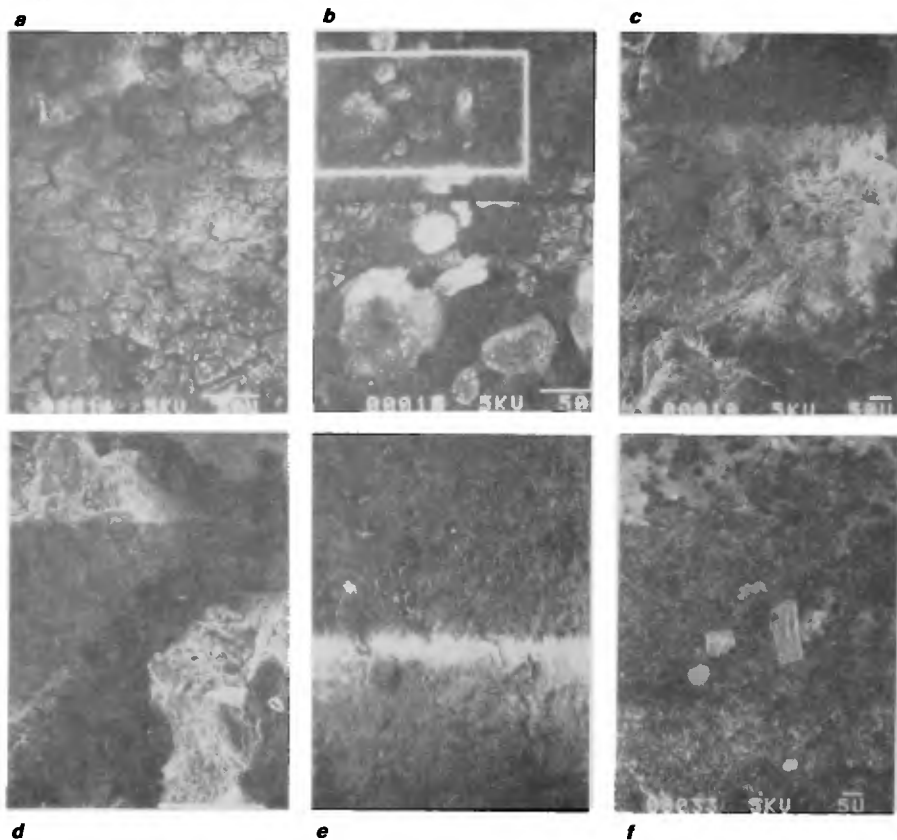
Parameter estimated	Value found (ppm)
pH	8.1
Sp. conductance at 25°C (microohms cm ⁻¹)	127.0
TDS	92.0
CO ₃ ²⁻	Nil
HCO ₃ ⁻	45.0
Cl ⁻	24.0
SO ₄ ²⁻	Nil
Ca ²⁺	18.0
Mg ²⁺	5.0
Na ⁺	7.5
K ⁺	0.56

Discussion

The principal factors of rock disintegration are hydrolysis, oxidation, carbonation, crystallization etc. In humid tropical regions such as southern India, hydrolysis and crystallization of salts in the pores are the predominant causes of stone decay. The pronounced mechanical disintegration observed about 1 m to 1.5 m from the ground level of Kailasanatha temple was mainly due to the crystal growth of soluble salts in the pores of monument stone ascended through capillary action, which exerted tremendous pressure causing exfoliation of the rock. The hydration and dehydration of these salts caused large flakes of the rock to split away. The mechanical disintegration of sandstone is also partly chemical since sometimes expansive force is provided by the hydration of certain minerals at the exposed surface of the rock. The danger associated with the presence of salts is rendered more acute by the fact that their deleterious action may continue as long as they remain in the material. Also the attack by sulphur dioxide gas is increased due to dampness maintained by salts. In the presence of water these salts also undergo hydrolysis, a process in which salt ions and water interact to yield an alkaline solution which attack many minerals, destroying their original properties.

Water containing dissolved oxygen and CO₂ is another principal reagent in rock decomposition. Soda and potash are released by hydrolysis of feldspar and go into the solution as carbonates. The resulting alkaline solutions can decompose many silicates at ordinary temperatures and pressures. It is difficult to establish the extent of physical damage caused by crystallization of salts and chemical dissolution caused by acid pollutants as both mechanisms may occur simultaneously. The weakest point in our current knowledge of rock decay is not the mechanism but the rate of deterioration due to the complex nature of the system in field conditions.

For the monument to survive, protection has to be afforded against not only meteoric water but also groundwater. Water-proofing can at best be provided around the foundations of walls and floors. In suitable cases, a high water-table can be lowered by employing special devices. For protection against



Figures 5a-f. Scanning electron photomicrographs. **a**, The lattice pattern with distinct demarcations ($\times 300$); **b**, The box at the upper half of the photograph ($\times 300$) has been enlarged further two times in the lower half, shows the presence of corroded quartz grains as a result of weathering; **c**, Abrased surface of crystals with their uneven and indiscipline distribution ($\times 100$); **d**, A deep crack ($\times 50$); **e**, Homogenous agglomeration of minerals in calcite cementing material ($\times 100$); **f**, Grains of quartz feldspar, etc. and their distribution in the granite stone ($\times 100$).

rain, 1-2% solution of polymethyl methacrylate in toluene has been found most effective since a thin film of this synthetic resin becomes insoluble and more resistant to moisture with time. To consolidate friable and highly weathered stone, a 5% solution of resin is most useful. Quartz and other grains, loosened by loss of natural binder are evenly coated and re-link to each other by the polymeric micro-layer.

At Kancheepuram rainfall is considerable for 4-5 months of the year and the average variation in temperature is of the order of 8-11°C. These conditions help in further degradation of the rock surface. Also a relative humidity of 70% with a temperature of 25-30°C is quite optimal for the cryptogamic plants to sprout and grow on the monument stone. The humus acid secreted by these plants slowly corrodes the minerals

present in the rock. Thus the binding between minerals is weakened and ultimately a tiny piece of stone gets detached from the parent rock.

To remove the salts, chemical treatment is of little use and washing with water at intervals is a better method. Laurie⁹ showed that washing removes salts which cause decay. Any soluble salts appearing on the surface should be brushed off gently before applying

water. On account of the deliquescent nature of alkali salts, washing is unlikely to be effective in complete removal of salts from the building stone. However, care has to be taken not to disturb any thin crusts of patina formed on the stone over a long period.

Conservation treatment

Preparation of paper pulp

For preparation of paper pulp, large size blotting paper sheets are torn into smaller pieces and soaked in water for two days. The supple and swollen bits are mashed into pulp with hands. The pulp is repeatedly washed with plenty of fresh water. The water soaked pulp is now transferred to a piece of cloth made into sack and twisted to squeeze the water out from the pulp after each washing. In this process, the salts present in the paper are almost washed. The pulp is again soaked in distilled water and stirred. After draining the excess water, the pulp is transferred to the cloth and squeezed. This process is continued until the filtered water stops giving milky colour if added with silver nitrate. A chloride free paper pulp is then ready for application. The used paper pulp can also be cleaned and re-used by this procedure.

Preparation of surface

The surface is made free from superficial accretions like dust, dirt, salt deposits etc. by dry brushing using very soft bristled brushes. The surface is now washed with ordinary water followed by gentle brushing and finally washed with distilled water. The salts present on the surface are washed away. The friable stone surface and patinated silica layer were first consolidated with 5% solution of polymethyl methacrylate in toluene before the preparation of the surface.

Application of paper-pulp

The squeezed paper pulp is soaked in minimum quantity of distilled water to get semi-solid consistency. A small quantity of pulp is applied on the surface with hands to enable it to adhere properly. Thus, a quarter inch thick paper pulp is uniformly applied on the panels. The principle of osmosis now sets in. The water from the pulp enters the pores of the stone dissolving the salts present. The salt concentration increases in the salt solution thus formed. To dilute this concentration, more water from the pulp enters the pores. Simultaneously, due to the prevailing heat and wind, water from the outer surface of the pulp facing atmosphere also evaporates at a high rate with the result more water is drawn from the pores of the stone. When water starts flowing towards the evaporating surface, it carries with it dissolved salts. Thus the salts inside the pores of the stone are removed and deposited on the interior surface of the pulp. After about two weeks, the dried paper pulp is removed from the surface. The repeated application of paper pulp is continued till the pulp is free from chloride ions. The paper pulp-treated panels were thoroughly washed with distilled water. After complete drying 1% solution of zinc silico fluoride was sprayed on the surface as fungicide. Lastly the entire area was preserved with 2% solution of polymethyl methacrylate in toluene. After this treatment the surface gains its original natural texture and appearance and the stone gains its compactness.

The vegetational growth from the Vimana of the temple was removed by applying a mixture of 3% aqueous solution of ammonia and 1% teepol (a non-ionic detergent) followed by gentle nylon brushing. After complete washing the surface was given fungicidal treatment and preserved with 2% solution of polymethyl methacrylate in toluene.

Conclusion

Marine salts are a permanent cause of natural pollution to building materials not only near the coast but even farther inland like Kancheepuram. Applying cellulose powder-based paste after consolidating the painted layer of silica with 5% polymethyl methacrylate in toluene has been found the best method for eliminating salts from the stone surface. This treatment can also be extended to hundreds ancient temples of Kancheepuram.

1. Amadari, M. L., Lazzarini, L. and Massa, S., Proceedings of the 1st International Symposium, Bari, 1989.
2. Abd El Hady, M. M., Publication of V International Congress on the Coptic and Nubian Studies, Warsaw University, Warszawa, Poland, August, 1983, pp. 1-9.
3. Alonso, F. J., Urdaz, J., Valdeon, L. and Esbert, R. M., *Mater. Construct.*, 1987, 37, no. 206, pp. 55-60.
4. Esbert, R. M. and Valdeon, L., *Bol. Geol. Min.*, 1985, 96, 81-88.
5. Winkler, Erhard, M., *Environ. Geol. Water Sci.*, 1987, 9, 85-92.
6. Rossi-Monarassi, R. and Tucci, A., *Stud. Conserv.*, 1991, 36, 53-58.
7. Lewin, S. Z., *Building and monuments*, National Academy Press, Washington, 1982, pp. 120-144.
8. Hughes, M. J., Cowell, M. R. and Craddock, P. T., *Archaeometry*, 1976, 18(1), 19-37.
9. Laurie, A. D., *Soc. Chem. Ind. J.*, 1925, 44, 18-92.

Acknowledgements. The author is grateful to Dr P. P. Naidu, of GSI, Bangalore, Dr P. K. Basu of GSI, Hyderabad, Messrs R. K. Sharma, and R. K. Chaturvedi of ASI, Dehradun, Dr K. V. Subbaiah and Dr Pandit Rao of BISR, Hyderabad, for help in experimental work. I thank Messrs K. G. Ragde and A. K. Bahadur for assistance.

Received 20 July 1992; revised accepted 2 December 1992.

M. Singh is in the Archaeological Survey of India, New Nallakunta, Hyderabad 500 044, India.