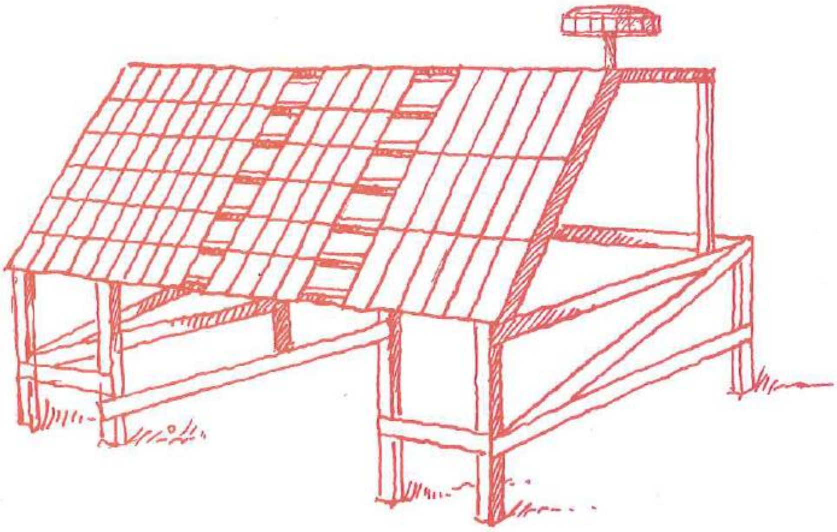
CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

UN/ECE INTERNATIONAL CO-OPERATIVE PROGRAMME ON EFFECTS ON MATERIALS, INCLUDING HISTORIC AND CULTURAL MONUMENTS



Report No 55:

Results from the 2005-2006 trend exposure programme. Corrosion attack of limestone after 1 year of exposure.

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Executive Summary

The International Materials Exposure Programme (IMEP) is part of the United Nations Economic Commission for Europe (UNECE) programme on the effects of trans-boundary air pollution. The programme began in 1987 and this latest phase began in November 1997. This phase is focuses on the possible synergetic effects of oxides of nitrogen (NO_x), sulphur dioxide (SO_2) and ozone (O_3) on a range of materials including steel, zinc, bronze, copper, painted wood, glass and calcareous stone.

This report details the experimental method and gives results of analysis of Portland stone samples after exposure in unsheltered positions at the 19 sites for 1 year as part of the in period 2005 - 06 in frame of the UN ECE ICP Working Group on Effects.

Tablets of Portland limestone have been assessed for changes in weight and the environmental conditions have also been recorded at or close to each site and are reported in a separate document. The results of the last exposure period are compared in this report to results found 10 years ago during the various phases of the IMEP.

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1. Introduction

The International Materials Exposure Programme (IMEP) is part of the United Nations Economic Commission for Europe (UNECE) programme on the effects of transboundary air pollution. The programme began in 1987 and this latest phase began in November 2005. This phase is focuses on the possible synergetic effects of $NO_{x,}$ SO_2 and O_3 on a range of materials including steel, zinc, bronze, copper, and calcareous stone in order to provide data to illustrate trends in the deterioration of materials over a period of nearly 20 years.

This report details the experimental method and gives results of analysis of Portland stone samples after exposure in unsheltered positions at 19 sites for 1 year. Tablets of Portland limestone have been assessed for changes in weight. The results of the last exposure period (November 2005 – November 2006) are compared in this report to results found 10 years ago during earlier phases of the exposure programme. Other materials exposed in this programme have been reported on separately by the responsible sub centres.

The results did not show the expected trends with many rates higher than expected. Possible reasons for this are discussed in the conclusions.

2. Description of the project

2.1 The stone type - Portland Limestone

This stone is an oolitic limestone from the Portland Beds of Upper Jurassic age (136 - 160 million years ago). The quarries are located on the Isle of Portland in Dorset, England. The tablets used in the exposure programme were obtained from the Whit Bed at Fancy Beach Quarry. The stone is a buff coloured shelly stone and petrological study shows the stone comprises ooliths and shell fragments surrounded by a calcite cement. The inter-granular porosity is between 22 and 23%. Portland has been quarried since the Roman period but became popular in the 17th century when Inigo Jones and Sir Christopher Wren used it in many buildings including St. Paul's Cathedral. Portland has remained popular with architects and builders because of its fine grain and durability, and because it weathers very evenly (Leary 1983).

2.2 Sample preparation

The stone tablets were sawn from blocks into tablets; 50 x 50 x 8 mm (±2 mm) in dimension. A 4 mm hole was drilled at the centre of the 50 x 50 mm dimension to allow fixing to a plastic support (carousel). Stone dust was removed by brushing with a nylon brush under running de-ionised water. The tablets were air dried for 2-3 hours before oven drying at 60°C for 3 hours and then 105°C overnight (16 hours). After the tablets had cooled they were weighed and sealed in plastic bags.

At the sites, listed in Table 1, stone tablets were fixed vertically to the arms of carousels (3 tablets per carousel) that were free to rotate about a vertical axis in order to eliminate directional effects. The carousels were exposed either completely unsheltered, thus receiving all weather conditions, or sheltered in a ventilated aluminium box which prevented rainfall reaching the tablets. A number of tablets, prepared as above, were not exposed but retained as pristine (control) samples.

2.3 Analysis of stone tablets

2.3.1 Weight changes

At the end of the exposure period the tablets were oven dried as before and re-weighed. Weight changes have been converted to recession rates in µm calculated as follows:

$$\mu m = \frac{100 \times (W_1 - W_0) \times 30.}{W_0}$$

W_0 = weight before exposure
W_1 = weight after exposure

The weight change percentage is

$$m\% = 100 \times (W_1 - W_0)/ W_0 ,$$

whilst the recession is

$$\mu m = (W_1 - W_0)/(A \times \rho) = m\% \times W_0 / (A \times \rho \times 100) = m\% \times V/(A \times 100)$$
$$= m\% \times 30$$

where V is the volume. Assuming a variance in the thickness of the tablets to be of the order of 0.5 mm then the error in the multiplier is of the order of 30 ± 2, which is far less than the error for other sources e.g. the triplicate weights.

Much of the cited literature on deterioration of natural stone is written in terms of a recession rate, as is the literature on natural erosion of rock slopes. Thus, on heuristic grounds quoting the recession rate is preferable to using the mass loss per unit area.

2.4 Environmental Conditions

The environmental conditions were measured at all the sites; temperature, relative humidity, sun radiation, SO_2, NO_2 and O_3 by diffusion tubes and annual rainfall. The rainfall was analysed for pH, conductivity and soluble salts.

3. Findings

3.1 Weight change of the unsheltered samples

The recession rate of the sheltered and unsheltered samples is given for each site in Table 1, for the years 1987-88, 1997-98, 2002-03, and 2005-06.

In general the unsheltered samples show a negative recession rate indicating some loss of material from the surface of the stone. However, the trends expected on the basis of the data collected for individual years from 1987 to 2003 were not followed with greater surface weathering at many of the site.

3.2 Conclusions and discussion

The results did not show the expected trends with many rates higher than expected. There seem to be two possible explanations for the unexpected results. The first is that the Portland limestone used in the latest exposure period not identical to the older material. BRE has many past results on the relationship between measured properties of Portland limestone and its weathering rates of the stone. On the basis of this experience a change in the rate by 40 - 50% would indicate a very significant change in the porosity and saturation co-efficient. As a check on this tests were undertaken on a two of the remaining samples of the 'old' stock and on two from the 'new' stock. The results are given in Table 2 (below).

Portland Type	Porosity	Saturation coefficient	Water Absorption	Density
Old	16.02	0.73	5.13	2271
Old	16.37	0.72	5.21	2263
New	18.58	0.63	5.35	2201
New	19.17	0.61	5.36	2186

The results show that new stone has a higher porosity but the lower saturation co-efficient which overall means it should be more durable. The values for the new stone are typical of the best Portland stone produced in the past. Overall BRE would expect both stone to have very similar rates of weathering.

The second possibility is that the climatic conditions were significantly different during the exposure period. This was known to be the case at some locations, for example the site at Chaumont (Switzerland) was covered with snow for many months. In this were the case then the provisional data for other materials would be expected to show similar trends and we believe this to be true. This should be investigated further once the other reports are completed – both those for the other materials and the environmental data.

Table 1 Recession data

Country	Name	1987-88 mm	1997-98	2002-03	2005-06 µm
		Unsheltered	Unsheltered	Unsheltered	Unsheltered
01 Czech Rep	Prague-Bechovice	-22.90	-6.00	-5.33	-7.75
03 Czech Rep	Kopisty	-19.40	-7.20	-7.91	-11.80
05 Finland	Ähtäri	-15.00	-4.80	-5.46	
07 Germany	Waldhof Langenbrüge	-9.10	-3.30	-7.00	
08 Germany	Aschaffenburg	-8.50	-6.30	-7.62	
10 Germany	Bottrop	-17.40	-11.70	-11.88	-15.2
13 Italy	Rome	-10.90	-6.00	-6.37	-8.87
14 Italy	Casaccia	-6.70	-6.00	-6.71	-9.85
15 Italy	Milan	-19.50	-9.00	-8.74	-15.09
16 Italy	Venice	-8.80	-9.60	-7.17	-9.58
21 Norway	Oslo	-11.70	-8.40	-7.31	-10.67
23 Norway	Birkenes	-17.00	-7.50	-7.66	-14.65
24 Sweden	Stockholm South	-14.00	-8.10	-7.29	-12.78
26 Sweden	Aspvreten	-6.80	-3.60	-4.30	-7.79
27 United Kingdom	Lincoln Cathedral	-9.90	-9.90	-7.63	
31 Spain	Madrid	-13.30	-3.30	-3.91	-8.11
33 Spain	Toledo	-6.20	-7.50	-5.82	-11.48
34 Russia	Moscow	-9.40	-9.00	-7.94	
35 Estonia	Lahemaa	-9.90	-5.40	-8.91	-10.65
36 Portugal	Lisbon	-6.90	-11.40	-10.59	
37 Canada	Dorset	-8.90	-6.30		-14.31
40 France	Paris	N/A	-8.70		-10.93
41 Germany	Berlin	N/A	-3.30	-2.00	-8.59
43 Israel	Tel Aviv	N/A			
44 (73&76) Norway	Svanvik	N/A	-6.60	-9.11	-9.79
45 Switzerland	Chaumont	N/A	-9.30	-9.04	-14.30
46 United Kingdom	London	N/A	-7.50	-9.03	
47 USA	Los Angeles	N/A			
51 Greece	Athens	N/A			