The cleaning and treatment of limestone by the 'lime method'. Part II. A technical appraisal of stone conservation techniques employed at Wells Cathedral

C.A. PRICE AND K.D. Ross

Introduction

Nobody who has examined the figure sculpture on the West Front of Wells Cathedral, both before and after conservation, can deny that there has been a dramatic change in its condition. As often happens in conservation, however, technical rationalisation of the change has lagged behind the skill of the craftsman who produces the change. When this investigation began in 1980, there was ample evidence that the lime treatment caused a major improvement in the condition of decayed Doulting stone. Nobody could say, on the other hand, which part(s) of the treatment had caused the change, how they had worked, nor how long the change would last. The aim of the investigation was, therefore, to provide a technical rationale for the treatment. The investigation also gave the opportunity to compare the performance of the lime poultice with two other cleaning techniques, air abrasion and water washing.

The experiment

Ideally, one would base the entire investigation on a single piece of stone, in order to eliminate variations in properties from one piece of stone to another. In practice, however, it was not possible to find one that was uniformly weathered and large enough to permit the necessary sampling. The investigation was therefore carried out on three pieces, cut from three mullions of the unglazed west cloister walk of the Cathedral. Each was of Doulting limestone, the stone from which the majority of West Front figures are carved. The mullions were believed to have been installed around 1470, and were equally dirty and decayed. The pieces cut out for experiment were 900 mm in length, with a cross-sectional area of about 180 cm².

The first stage of the experiment was to clean the mullions, using a lime poultice, air abrasion or water washing. The design of the experiment (Fig. 1), permitted direct comparison of any two techniques on a single piece of stone. A central portion, approximately 20 mm in thickness, was

* Clifford Price is now the Head of the Ancient Monuments Laboratory at the Historic Buildings and Monuments Commission (English Heritage). Formerly a Principal Scientific Officer at the Building Research Establishment, he was instrumental in setting up the Stone Section at the Building Research Station and in pioneering research work into stone consolidants.

Keith Ross is a Head Scientific Officer at the Building Research Station (BRE) and is still involved in the stone selection and research programme.

lime poultice
control
air abrasive
control
water
air abrasive
control

FIG. 1. The design of the experiment permits direct comparison of any two cleaning techniques on a single mullion.

water

¹ Schaffer, R.J., The Weathering of Natural Building Stones.
Building Research Special
Report No. 18, 1932.
Reprinted BRE 1972.

first cut out using a dry saw and served as a control. The remaining six pieces were then cleaned by the conservation team—two pieces for each technique. Every effort was made to ensure that the cleaning was carried out in a realistic manner. The lime poultice cleaning and the air abrasive cleaning were carried out on the scaffold alongside a figure that was being cleaned by the same technique. The water washing, normally used for the 'architectural stonework' but not for the figure sculpture, continued until the stone was clean and lasted around two days.

When cleaning was completed and the stone had dried (where necessary) a 20 mm slice was cut with a dry saw from the centre of each of the six pieces. This slice was set aside for laboratory examination. Of the two pieces that remained from each of the original six pieces, one piece was treated with around 40 applications of limewater whilst the other was left untreated. The lime watering was carried out by the conservation team in exactly the same way as the lime watering of the figure sculpture.

When the lime watering was completed, a 20 mm slice was cut from the centre of each of the lime watered pieces and set aside for laboratory investigation. One of the two remaining pieces was covered with shelter-coat. The blocks that had not been lime watered were simply cut in half and one half was covered with shelter-coat. A sample for laboratory study was then cut from each of the shelter-coated pieces, and all the remaining pieces were exposed to the weather. Their condition will be monitored over the next few years. This seemingly complicated procedure, illustrated for a single mullion (Fig. 2), enabled each part of the conservation treatment to be studied, either in isolation or in conjunction with other parts. 'End effects' were eliminated in the cleaning and lime watering stages by cutting the specimens for laboratory study from the centre of each treated piece. This precaution was not necessary in the shelter-coat stage.

Laboratory investigation of specimens

Each 20 mm slice of mullion was sampled (Fig. 3). All cutting was done dry, to prevent any redistribution of calcium sulphate or calcium hydroxide.

Distribution of calcium sulphate

The majority of investigators agree that calcium sulphate plays a major role in the decay of limestones, the calcium sulphate being formed by reaction of the limestone with sulphur oxides in the air. There is remarkably little understanding, however, of the precise mechanisms by which the calcium sulphate causes decay, and little can yet be added to Schaffer's summary of 1932.

On first sight, it would appear to be beneficial to the stone if all the calcium sulphate could be removed from it. However, this is not

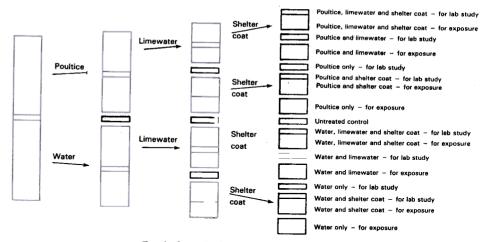
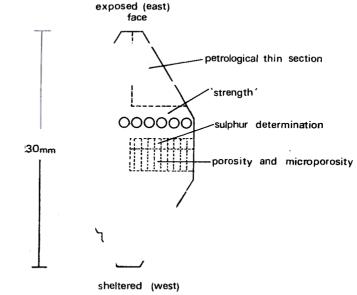


Fig. 2. Stages in the treatment of one mullion.



face

Fig. 3. Sampling of mullion sections.

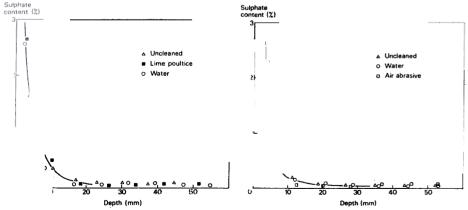
² This experience led to a refinement of the technique for washing architectural stonework, in which water was sprayed onto the stone for only a few seconds at a time, with intervals of several minutes in between. The spray was controlled either by a time switch or by electronic sensors placed on the stone. This refinement enabled the stone to be kept wet, thus softening dirt, without the calcium sulphate being bleached out.

³ The data in Fig. 4 should strictly be shown in histogram form, but the graphical representation is much clearer.

necessarily so. When stone is in a very advanced stage of decay, the calcium sulphate may actually be serving to bind the stone together. If the calcium sulphate were to be removed, the stone would disintegrate altogether. This phenomenon was in fact observed at Wells, when conventional water mist sprays were used to clean highly undercut architectural detail. The prolonged washing leached the calcium sulphate from the stone, which was reduced to a soft mass.² One must conclude that removal of the sulphate is not necessarily beneficial, despite the fact that one would prefer the calcium sulphate not to be there in the first place.

The effects of the three cleaning techniques on sulphate distribution are shown in Fig. 4, which gives the results for two of the mullions. The results show beyond doubt that none of the cleaning techniques has any influence on the quantities of sulphate contained within the stone. It should be remembered, however, that these results relate to specimens which are typically 7 mm in thickness; they are thus the average sulphate content within a 7 mm specimen. If there were to be any redistribution of the sulphate within such a specimen, it would not be discernible from these results. Nevertheless, the results clearly refute any claim that the lime poultice serves to draw calcium sulphate out of the depth of the stone.³

The situation is different when one examines the amount of sulphate on the surface of the stone. Table 1 contains the results of sulphate analyses on scrapings from the surface of the various samples. In both cases of water washing, the washing removes more than 80% of the sulphate skin. The effects of the air abrasive and the lime poultice, on the other hand, are more variable. In one case, the air abrasive reduced the sulphate content



Variation of sulphate content with depth. Analysis was by carbon/sulphur combustion, all sulphur being taken as sulphate.

Table 1. Sulphate content of surface scrapings, following the initial cleaning stage.

	Cleaning technique	Sulphate content (sc
Mullion 1	lime poultice	26.5	
	(control)	28.0	
	air abrasive	22-1	
Mullion 2	lime poultice	4-4	
	— (control)	26.0	
	water	4.8	
Mullion 3	air abrasive	12.8	
	— (control)	26-3	
	water	3.8	

by 21%; in the other case by 51%. The lime poultice reduced it by 5% in one case and by 83% in the other—an even greater reduction than was caused by water washing. The variability of the results is not surprising, for some areas of stone will come clean more readily than others. In the case of the lime poultice, in particular, water is used to assist cleaning after removal of the poultice, so one might expect that areas that had required a good deal of washing would give results similar to those for water washing alone.

The results of Table 1 are borne out by examination of petrological thin sections. The sulphate skin is largely absent from samples that have been water washed, whereas it is present in variable amounts in those that have been cleaned by air abrasive or lime poultice.

These data confirm that water washing is potentially harmful to the stone, for it can remove the sulphate that binds surface grains together. The air abrasive and the lime poultice, on the other hand, permit a reduction in the sulphate skin without disrupting the stone below. This will facilitate the subsequent absorption of limewater but will also make the stone more vulnerable to further attack by acid rainwater unless the protective shelter coat is applied. One advantage of the air abrasive over the lime poultice is that the air abrasive is more selective: it is possible to clean around traces of pigment, for example, without affecting the pigment itself.

Deposition of calcium bydroxide

This part of the investigation was aimed at detecting any calcium hydroxide or calcium carbonate that had been deposited in the stone. The lime poultice consists of calcium hydroxide, and the limewater is a solution of calcium hydroxide. Either the poultice or the limewater could thus lead to the deposition of calcium hydroxide, which would

subsequently react with carbon dioxide in the air to form calcium carbonate. Ultimately, the calcium carbonate would react with sulphur dioxide in the air to form calcium sulphate.

The search for calcium carbonate/hydroxide was based mainly on examination of petrological thin sections, in the expectation that this would reveal the precise points at which deposition had occurred and would also give some indication of whether the deposition had occurred largely at the surface or in depth. In the event, the search was disappointing; in the majority of specimens, no deposits could be seen in the treated specimens (either after poulticing or lime watering) that could not also be seen in the controls.

The failure to detect calcium hydroxide/carbonate does not necessarily mean that no carbonate or hydroxide has been deposited or that the lime treatment is worthless. It is possible that very small quantities of carbonate/hydroxide could have a marked effect on the strength of the stone if deposited in just the right places, and that the petrological examination has not been sensitive enough to detect such deposits. Alternatively, it is possible that the calcium carbonate/hydroxide has already been converted to calcium sulphate, which is indistinguishable from pre-existing calcium sulphate.

Porosity and microporosity

The porosity of a stone is defined as the volume of the pores that it contains, expressed as a percentage of the bulk volume of the stone. The 'microporosity' gives a broad indication of whether the pores are mainly coarse or fine. A high microporosity indicates a high proportion of fine pores and is normally associated with low durability; conversely, a low microporosity indicates a high proportion of coarse pores and is normally associated with high durability. In the present investigation, it is not so much the absolute values of microporosity that are of interest as the relative values, before and after treatment. Any marked change in the microporosity would indicate a significant change in the pore structure of the stone, with a consequent change in durability.

A representative selection of the results is depicted in Figs 5 and 6. As one would expect, particularly in the absence of major deposits in the petrological thin sections, neither the poultice nor the limewater has any discernible effect on the overall porosity of the stone.⁵ The microporosity data, likewise, show no effects attributable to the lime treatments.

Strength

One of the main benefits claimed for the lime treatment is the increase in strength that it brings about. Strength measurements, before and after treatment, are therefore essential to any assessment of the treatment. However, strength measurements are normally carried out on large cubes

70 O Uncleaned 60 a water/limewater △ poultice 50

depth (mm)

microporosity (%)

Fig. 5. Variation of porosity with depth.

porosity (%) O uncleaned water mater/limewater △ poultice 15 depth (mm)

Fig. 6. Variation of microporosity with depth.

of stone (eg 80 mm side), and many measurements must be made in order to eliminate statistical fluctuations. Such measurements are clearly impossible in the present instance, and a technique attributed to Butterbaugh⁶ was tried instead. This entailed placing the stone in the jet of an air abrasive gun and measuring the size of the hole that was made in a given time.

The abrasive used was a silica sand of 100 FG mesh. The gun had a 5 mm nozzle and was operated at 40 psi. It was held in a clamp 100 mm away from the surface of the stone. A thin sheet of metal, with a 7 mm diameter hole drilled in it, was placed on the surface of the stone. The gun was operated for 2 minutes, and the metal sheet was then moved on to another position. In this way, it was possible to make a line of holes, at approximately 10 mm centres, from the outer edge of each mullion slice

Microporosity is defined the volume of water ined (expressed as a pertage of the available pore ce) when a suction equivato a 6-4 m head of water is lied to the specimen. The cept is discussed in The ction of Natural Building e, Building Research ablishment Digest 269. The detailed test proure is given in *Proceedings of* International Symposium on Deterioration and Protection tone Monuments, Unesco/R-M, Paris, 1978. Vol. 5, t I. 4.

Bear in mind, when exning the data, that the e itself is not uniform and fluctuations will inevitaoccur from one part of the e to another.

⁶ Phillips, M.W., Acrylic precipitation consolidants. IIC Congress on Science and Technology in the Service of Conservation, Washington

to the centre. The size of each hole was measured by filling it level with 120 mesh carborundum grit, weighing the grit and converting to volume.

Examination of all the mullion slices by this technique is not yet completed, but the results for one of the mullions are shown in Fig. 7. Disappointingly, the results are inconclusive. There appears to be a lot of scatter, which is not surprising in view of the inhomogeneity of the stone. Many more results would be required in order to confirm the statistical validity of any apparent trend and even in the 'best' instance, the size of the outer-most holes after lime watering is not very much lower than those of the control.

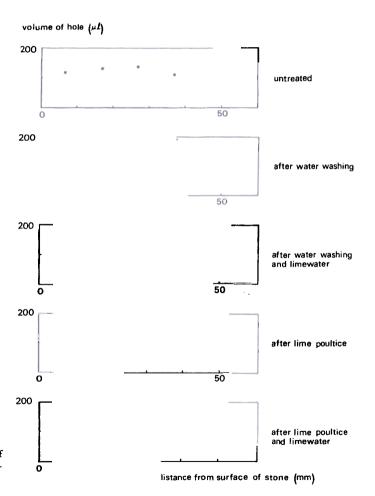


Fig. 7. Estimation of strength by abrasion resistance.

The shelter coat

Examination of the specimens treated with shelter coat has not yet begun.

Consolidation of crushed stone

In the absence of conclusive data on strength, an attempt was made to consolidate crushed stone with limewater. Clearly, any consolidation so achieved would represent an increase in strength, since the initial strength was zero. Two types of stone were used, Doulting limestone and Monks Park limestone, the latter being an oolitic stone mined near Bath. A silica (Ham River) sand was also tried. In each case, a carefully graded mix was prepared, in accordance with British Standard BS 1200. The proportions retained by standard meshes were as follows: 2.36 mm, 10%; 1.18 mm, 20%; 600μ , 20%; 300μ , 20%; 150μ , 15%; 10% passed a 150μ sieve. The mixture was placed, while moist, into the filter funnel depicted in Fig. 8, dried and weighed. The tip of the filter paper was then dipped into limewater until the crushed stone was all visibly wet; this took five to ten minutes. This procedure was adopted in order to avoid the fine particles in the mixture from being washed to the bottom, as would have happened if the limewater had been poured in from the top. The stone was then

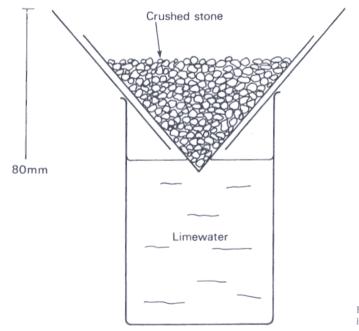


Fig. 8. Attempted consolidation of crushed stone.

allowed to dry at room temperature. The drying period was never less than 24 hours and was usually several days. The cycle of wetting and drying was repeated 30 times, covering a period of 6 months. On each occasion, a control specimen was treated with distilled water.

At the end of the experiment, the Doulting and Monks Park specimens had increased weight by 0.38 and 0.40% respectively. The sand had increased weight by 0.22%. The control specimens had not changed weight significantly.

Despite the increase in weight, none of the lime watered specimens showed any significant consolidation. All of them crumbled at the slightest pressure from a spatula. The Doulting specimen was perhaps marginally stronger than its control, but the Monks Park specimen was, if anything, even more friable than its control. Certainly none of the specimens showed the slightest degree of useful consolidation.

It is generally assumed that any consolidation would be achieved by carbonation of the calcium hydroxide, in a manner analagous to the hardening of lime mortars. Lime mortars harden when carbonation yields an interlocking mass of calcite crystals which binds the aggregate particles together. By comparison with a limewatered sample of stone, however, the amount of calcium hydroxide available for carbonation in a lime mortar is enormous. The reason for the failure of the limewater to achieve consolidation in this experiment may simply be that insufficient calcium hydroxide is deposited in the stone.

An alternative suggestion was contained in a Building Research Station Digest published in 1959.8

It is clear that the mechanism by which limewater can consolidate porous building materials is not yet understood. There are certainly instances where useful consolidation has been achieved, especially with lime plasters, but equally there are some instances where there has been no apparent effect. It is hoped that the present study will stimulate other workers to a further investigation of the general problem.

Conclusions

- 1. A lime poultice, and associated washing, does not serve to extract calcium sulphate from the depth of the stone.
- 2. A lime poultice, and associated washing, can reduce or remove the calcium sulphate skin on the surface of the stone. This may assist the subsequent absorption of limewater, but also makes the stone more vulnerable to attack by acidic rainwater unless a protective shelter coat is applied.
- There is no evidence that a lime poultice serves to consolidate friable stone.
- 4. A lime poultice should be regarded as one of a range of possible cleaning techniques (eg clay poultice, air abrasive), each of which has

- its own strengths and weaknesses. It should not be regarded as a technique of unique stature.
- 5. On the basis of the laboratory experiments described, there is no conclusive evidence that multiple applications of limewater serve to consolidate friable limestone. This aspect is considered to require further investigation.
- 6. Despite these rather negative findings, the lime technique can undoubtedly produce a dramatic change in the condition of decayed limestone. It is possible that part of this change, at least, is attributable simply to the meticulous care and attention which the stone receives, as described in Part I—principally the painstaking preparation of the stone, and the placing of carefully designed mortar. In view of the evident benefits of the technique, the authors have recommended its continued use at Wells.

Acknowledgments

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Resumen

Cuando en 1980 empezó la investigación que se describe en este artículo, existían amplias pruebas de que el tratamiento calizo producía grandes mejoras en la condición de piedra Boulting dilapidada. Por otra parte, nadie podia indicar qué parte del tratamiento había producido el cambio, ni de qué modo, ni cuánto tiempo iba a durar. Por consiguiente, el objeto de la investigación era el de proporcionar las razones técnicas del tratamiento. También facilitó la oportunidad de comparar los resultados del cataplasma de cal con otros dos agentes limpiadores, abrasión por aire y lavado de agua.

Las conclusiones son las siguientes:

1. Un cataplasma de cal, junto con lavado, no sirve

- para extraer sulfato de calcio de las profundidades de la piedra.
- 2. Un cataplasma de cal, junto con lavado, puede reducir o eliminar la capa de sulfato de calcio en la superficie de la piedra. Esto puede facilitar la subsiguiente absorción de agua de cal, pero también hace a la piedra más vulnerable al ataque de lluvia ácida, a menos que se aplique una capa protectora.
- No hay pruebas de que un cataplasma de cal sirva para consolidar piedra friable.
- Un cataplasma de cal debe ser considerado como una de varias técnicas posibles de limpieza (v.g., cataplasma arcilloso, abrasión por aire), cada una

- ⁷ Lea, F.M., The Chemistry of Cement and Concrete, 3rd edn, London 1970, 252. ⁸ Stone Preservatives, Build-
- ing Research Station Digest 128 (First series), 1959. The Digest stated that 'appreciable strengthening effects are now reported to have been obtained on friable stone by repeated applications of clear limewater'. After stating that 'repeated applications of limewater in the laboratory had no measurable effect on the strength of friable marble', the Digest suggested that any consolidation that might be achieved in situ might 'owe as much to the solution and redeposition of calcium sulphate already present in the stone as to the lime introduced into it'. This tallies with the later observation that distilled water could sometimes achieve as much consolidation as limewater. (Clarke, B.L. and Ashurst, J., Stone Preservation Experiments, BRE Ig 72).
- ⁹ Clarke and Ashurst, op.

de las cuales posee sus ventajas y desventajas. No debe ser considerado como técnica sin par.

5. Como resultado de los experimentos de laboratorio descritos, no hay pruebas definitivas de que aplicaciones múltiples de agua de cal sirvan para consolidar piedra caliza friable. Se considera que este aspecto requiere mayor investigación.

6. A pesar de estos resultados más bien negativos, el método calizo sin duda puede ocasionar un cambio espectacular en la condición de la piedra caliza dilapidada. Es posible que, al menos en parte, el cambio se deba sencillamente al cuidado y atención meticulosos que recibe la piedra, como se describio en la primera parte; sobre todo, la minuciosa preparación de la piedra y la colocación de mortero cuidadosamente elaborado. En vista de los claros beneficios de la técnica, los autores han recomendado que siga utilizándose en Wells.

Résumé

Lorsque les recherches décrites dans cet article commencèrent en 1980, il y avait de nombreuses preuves que le traitement de la pierre calcaire avait abouti à une nette amélioration de la pierre abîmée de Boulting. Mais personne ne pouvait dire quelle partie du traitement avait été efficace, comment elle avait opéré ni combien de temps l'amélioration durerait. Le but de l'enqête était donc de fournir une explication rationnelle au traitement. Elle fournit aussi l'occasion de comparer l'efficacité de l'enduit de chaux avec deux autres traitements, l'abrasion par air et le lavage à l'eau.

Les conclusions sont les suivantes:

 L'enduit de chaux et le lavage qui l'accompagne ne servent pas à extraire le sulphate de calcium de la profondeur de la pierre.

2. L'enduit de chaux et le lavage qui l'accompagne peuvent réduire ou supprimer la peau de sulphate de calcium sur la surface de la pierre. Ceci peut favoriser l'absorption ou lait de chaux mais aussi rend la pierre plus vulnérable à l'attaque des pluies acides à moins q'un enduit de protection ne soit appliqué.

3. Il n'y a pas de preuve qu'un enduit de chaux serve à consolider une pierre friable.

4. L'enduit de chaux doit être considéré comme l'une des techniques de nettoyage possibles (par ex. un enduit d'argile ou l'abrasion par air) qui ont chacune leurs avantages et leurs désavantages. Ce n'est pas une technique particulièrement efficace.

5. A la lumière des expériences de laboratoire décrites ici, il n'y a pas de preuve définitive que des applications répétées de lait de chaux soient utiles pour consolider une pierre friable. Cet aspect du traitement demande d'autres recherches.

6. Malgré ces conclusions plutôt négatives, la technique de la chaux peut certainement produire de remarquables résultats. Il est possible que ces résultats soient en fait dûs au soin méticuleux auquel la pierre est soumise—comme le décrit la première partie de cet article—en particulier la préparation très soignée de la pierre et l'application d'un mortier spécial. Etant donné les avantages évidents de cette technique, les auteurs ont recommandé qu'elle continue à être utilisée à Wells.