Urban pollution and stone decay

Stone is one of the most enduring of building materials. But since the industrial revolution it has been under attack from a harshening atmosphere created by pollution. The results of that are explored here by Carlota Grossi, Barry Hunt and Sarah Smart of STATS Consultancy.

Detail of one of the entrances to the Cathedral of Oviedo. A pollution black crust affects the upper stonework while decay associated with salts and dissolution by water can be seen to the right where the stone has been cleaned.

THINK OF the major historical buildings around the world, from the Pyramids outside Cairo, the Parthenon in Athens and the Coliseum in Rome to the Tower of London. The most common factor in their survival is the stone with which they were built. Most modern developments recognise the popular view of the 'rock of ages'. By using stone a feeling of austerity and permanence is imparted to the beholder.

Unfortunately, the most common factor in the destruction of these monuments and just about every other stone edifice in existence is atmospheric pollution. While natural weathering processes are often viewed as the great leveller of stone, it is the combination of these and pollutants borne by the air that is at the heart of most stone deterioration. Many ancient monuments around the world survived centuries of natural weathering intact but have suffered since the advent of modern atmospheric pollution.

Look around the great cities at even relatively new buildings employing stone in the facades and the most notable alteration is the soiling of surfaces.

With time, a crust may develop, partly of dirt, partly of reacted stone. The stone is weakened and the crust may detach to expose new stone for further reaction. Unremoved, some types of crust may actually protect stone from further reaction and in some situations it is advisable to leave the crust alone since removal by ill-advised cleaning / restoration can result in disastrous decay.

The problems of atmospheric pollution are at their worst in urban environments. By understanding the processes that cause stone decay there is some chance of slowing, and possibly even halting, its progress.

Importantly, such knowledge might be used in the selection of stone for modern construction purposes to avoid the unsightly alteration that blights so many buildings so early in their lives.

First we must look at the different forms of atmospheric pollution and their effects, then consider their impact on building stone.

Atmospheric pollution is the introduction into the atmosphere of substances or effects that are potentially harmful to, or interfere with, man's (and other species') use of the environment[1]. Pollutant emissions into the atmosphere can arise from natural sources, such as volcanoes and forest fires, or human activities, including the burning of fossil fuels, especially in vehicle engines.

Pollutants are termed either primary (when they are created directly) or secondary (when they arise indirectly by chemical

Table 1. Emmission of primary polutants, 1997 (thousand tonnes)

Source	Black smoke	SO_2	NO_x	CO
Electricity generation	18.4	1025.2	370.0	70.3
Commercial industrial	85.0	564.1	378.2	859.7
Road traffic	183.9	27.5	882.9	3797.0
Domestic and Other	27.1	43.0	203.7	362.9
Total	314.4	1659.8	1834.8	5089.9

Source: Department of the Environment, Transport & the Regions (DETR)

For comparison

Total in 1989	512	3699	2700	6522

Source: Clarke, 1995.

processes in the atmosphere)[2].

Pollutants created by human activity arise from three major sources[2]:

- stationary combustion
- mobile combustion
- non-combustion.

Stationary combustion is typically a combination of domestic and industrial burning and can be the source of carbon dioxide (CO_2), carbon monoxide (CO), particles (soot or ash), hydrocarbons, sulphur oxides (SO_x), nitrogen oxides (NO_x) and hydrogen chloride.

Mobile combustion sources such as the internal combustion engines of road vehicles can give rise to different gases such as CO, NO_x and hydrocarbons. Diesel engines are an important source of soot from impurely burnt fuel and provide a significant component of urban pollution. Particles rich in lead or sulphur typically originate from mobile combustion sources and produce a variety of detrimental effects on human health.

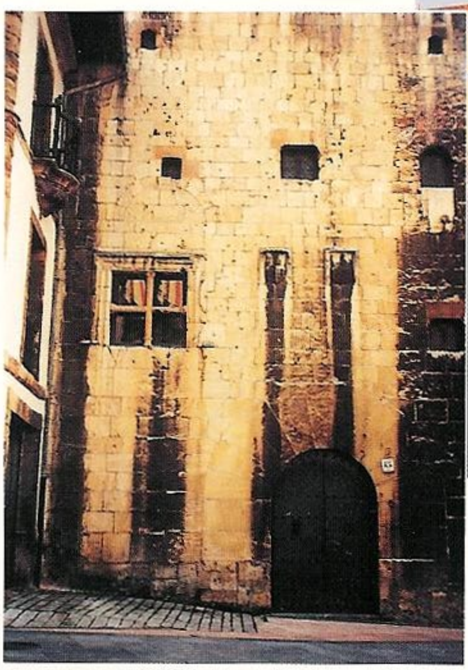
Sources of pollution where combustion is not a function principally involve the activities of heavy industry. Gases may originate from sulphuric or nitric acid plants, paints and minerals processing. In urban environments, some large construction sites may persistently produce large quantities of airborne particles, or dust.

Table 1 shows the emission of primary pollutants by source type in the UK for 1997. Power stations account for the bulk of SO_2 emissions along with a substantial chunk of the NO_x emissions, although the output of both from power stations has fallen substantially in the past decade. Road vehicles account for a lot of pollution. Diesel engines account for most of the NO_x and contribute 100 times more sooty particles than petrol engines, although petrol engines account for most of the CO emissions.

Atmospheric particles can be divided into three main groups according to their size:

- Very small particles (<0.1μm [micron]), known as 'Aiken nuclei', originating from homogeneous or heterogeneous condensation. This fraction is rich in particles in which sulphur is the main element and can represent a high percentage of the sulphur deposited on stone[3]. Soot or elemental carbon, responsible for soiling of buildings, can also be classified in this category.
- Particles of 0.1-10μm, which are stable suspensions and can be transported long distances by wind[4].
- Particles >10μm, which are known as sedimentable particles because they remain air suspended only for a relatively short period of time. These larger particles can be generated by industrial processes, road vehicles and construction and can include dust raised by the wind and sea salts[2].

Above. Tower of the Cathedral of Oviedo in north-west Spain. It was mainly built using a medium density limestone. A black crust developed as a result of pollution.



Left. An historic house in Oviedo built of the same stone as the cathedral. Pollution black soiling has developed in areas more sheltered from the direct action of rainwater.

Atmospheric levels of smoke and sulphur dioxide are decreasing mainly because of the reduction in the use of coal as a source of energy and cleaner burn at power stations. However, emissions of nitrogen oxides and carbon monoxide (NO_x and CO) continue to be high as a result of increasing road traffic.

The term 'acid rain' has nowadays come to be used to mean almost anything to do with air pollution, whether or not 'rain' is actually involved. However, 'acid rain' strictly refers to rainfall acidification by the conversion of sulphur dioxide and nitrogen oxides into sulphuric acid and nitric acid, respectively.

More than 50% of the

Clean air raises green issues

Professor Geoffrey Allen and some of his students from the Interface Analysis Centre of the University of Bristol spent the holiday weekend at the end of May giving a practical demonstration of chemistry seven stories up on the Portland limestone façade of new offices close to the Bank of England in London.

The architects, who prefer that they and the building should not be identified, contacted the university for help when the stone under a copper roof developed green streaks.

Geoff Allen investigated. The cause of the staining was, ironically, cleaner air – or, at least, air with different proportions of pollutants.

Sulphure dioxide (SO_2) in the atmosphere turns copper its familiar green colour from its shiny golden newness. This is the colour architects expect and want copper roofs to turn.

The green colour is produced by the copper sulphate brochantite ($CuSO_4.3Cu(OH)_2$) created by the copper reacting with SO_2 in the air. It gives the metal a protective coating which prevents further corrosion as well as producing the green colour.

Lately, however, levels of SO_2 in the atmosphere have been falling in line with Government targets largely due to lower emmissions from power stations.

Allen discovered that as a result of the changes in the atmosphere copper roofs now contain a different copper sulphate, antlerite ($CuSO_4.4Cu(OH)_2$), which is slightly more soluble than brochantite. When it rains, some of it is dissolved. In London it is this dissolved antlerite causing the green, run-off staining, he says.

Such staining has proved resistant to cleaning. At the Albert Memorial, where the run-off staining came from statues above the stone, various cleaning compounds were tried without initial success. Eventually the stains were removed using a combination of poultice materials applied up to six times in any one area (see *Natural Stone Specialist*, March issue).

Allen says his treatment will work after three applications. It is spread on as a white paste. It hardens and turns yellowish in less than a day and is then removed.

Exactly what the treatment is and how it works he is not prepared to divulge. He will only say: "We just applied some scientific testing." He adds that he would like to patent the formula. "We have something new, there's no doubt about it. But precisely where we go from here I don't know."

A product has been developed in association with the company Permagard Products in Bristol, who, says Allen, were invaluable in turning the experimental material into a commercial prospect, especially in relation to the Coshh regulations involved in production. The material is being sold under the name of Kemlock.

Allen says he is now developing a similar product for the treatment of iron stains.

Of course, staining will recur if the source of it is not eliminated and Geoff Allen suggested to his clients in London that they put up guttering to stop the rain running off the roof onto the stone.

An interesting aside to the changes in the atmosphere is that nitrous oxides (NO_x) from car exhausts are constituting a greater proportion of the pollutants. As a result, copper roofs could turn brown in the future rather than green.

Green staining of stone by dissolved copper sulphates is the result of cleaner air and is difficult to remove. But Professor Geoff Allen of the University of Bristol believes he has developed an answer.

- For more information contact Prof Geoff Allen, Interface Analysis Centre, Oldbury House, 121 St Michael's Hill, Bristol BS2 8BS. Tel: 01179 255666.

acidic component of acid rain is SO_2, while 20-30% is NO_x. Various chlorine-based compounds make up much of the remainder. *The Dictionary on Environmental Science and Technology*[1] gives the following definitions:

- Acid precipitation: rainfall or snow with a pH lower than 5
- Acid mists: fog, mist or low cloud in which the water has a pH lower than 5
- Acid deposition: total deposition of hydrogen ions or acid-forming compounds, eg SO_2 and NO_x, by both wet and dry deposition. When a pollutant impacts on to soil, water or vegetation at the Earth's surface, this is termed 'dry deposition'[1]. The term 'wet deposition' is used to describe pollutants brought to ground either by rainfall or snow[2].
- Acid rain: precipitation and other deposition pathways that are more acidic than pH 5.

Pollution and stone decay

The decay of building and monumental stones in urban environments can be related to the deposition of pollutants in the form of acidic gases and particulate matter on the stone surfaces.

Gases react with stones, most notably in the case of carbonate-bearing stones such as limestones and some varieties of sandstone. Particulate matter contributes to the soiling of the stone and can accelerate the oxidation of sulphur dioxide (SO_2) to sulphate (SO_4^{2-}).

The product of the reaction of the sulphur dioxide with carbonate stone components is calcium sulphate in the hydrous form known as gypsum. The growth of this gypsum within the stone can exert pressures that physically destroy the stone fabric in a variety of ways.

Dry deposition of SO_2, mainly coming from the combustion of fossil fuels, and the subsequent oxidation into sulphate is a prevalent decay mechanism in urban areas.

Other gases present in urban atmospheres, such as NO_x, can also deposit on stone surfaces[5]. In the presence of moisture, NO_x can enhance SO_2 oxidation[6].

In the case of carbonate- ➪

Slate roofing in central London showing discolouration due to reaction with some acidic components of rain. There are also dirt deposits.

bearing building stones, chemical degradation is thought to be caused by three mechanisms[7]:

- dry deposition of acidic species
- dissolution by acidic species in rainwater
- dissolution by unpolluted water.

The rate of degradation also depends on a variety of basic stone properties, particularly the pore structure, which will determine the rate of take-up of liquids and gases. The type of carbonate also determines the rate and type of dissolution and the products resulting.

The rate of uptake of SO_2 by stone is strongly affected by the relative humidity within the stone[8] and, therefore, dependent upon its hygroscopic properties. The potential moisture uptake increases with the higher specific surface area produced by decreasing pore size[9]. The presence of hygroscopic salts within stone also contributes to the maintenance of a higher natural moisture content, making SO_2 uptake and oxidation easier[10].

Stone decay by particulate matter (solid particles) is mainly due to the catalytic effect in the oxidation of SO_2 to sulphate (in the presence of moisture) and the soiling of stone surfaces.

Black soiling is mostly caused by the deposition of carbonaceous ash residues from combustion. Nowadays, diesel engines are the main source of carbon[11]. Porosity and surface roughness are some of the material characteristics that determine particulate deposition.

Products generated from reaction between stone and atmospheric pollution can also promote deterioration of the materials. These products are mainly soluble salts, sulphates being probably the most characteristic although chlorides and nitrates may also be found.

Salts can contribute to decay by leading to cycles of crystallisation-dissolution; cycles of hydration; differential thermal expansion to the host material; salt textural or structural changes.

The role of rainwater in the deterioration of stone is greatly underestimated. Water alone can dissolve and move salts around and will be at the heart of all the mechanisms driving stone decay.

In summary, stone decay is the result of a combination of a complex variety of environmental agents and stone characteristics. Carbonate-bearing stones are by far the most sensitive to the effects of pollution, although in urban environments, gypsum (mainly) and in smaller proportions other salts such as nitrates and chlorides are found on stone surfaces even when the stone is non-carbonate[12].

The open porosity and specific surface area of a stone influence moisture transfer and determine to a great extent the deposition of pollutants on the stone and the reaction of the stone with those pollutants. Also, stone surface roughness can control the deposition of soiling and / or reactive atmospheric particles on the stone.

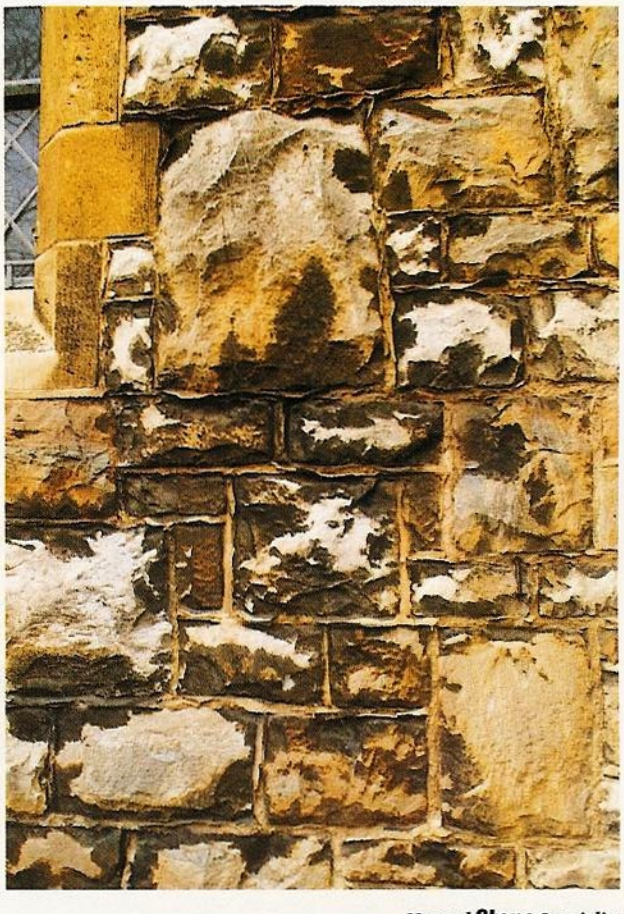
The reaction products are mainly soluble salts that can migrate to the interior of the stone and can contribute to its deterioration. They can also help to maintain high humidity inside the stone, enhancing the deposition of further pollutants.

Table 2 lists the major categories of stone used in building construction and their potential for decay as a direct result of pollution.

Table 2. Common stone types and their performance when subjected to pollution

Stone Type	Common Usage	Basic Characteristics	Major Changes	Damage
Granite	Cladding, some ashlar	Siliceous (acid resisting), very low porosity	Light soiling where polished, heavier soiling when textured	Little, deposits often removable without permanent damage
Marble	Cladding (not recommended), statuary	Typically carbonate-bearing, very low porosity	Usually polished, light soiling, loss of polish, long term growth of crusts	Loss of polish by acidic etching, little other permanent damage
Sandstone (siliceous)	Ashlar, paving	Siliceous, low to high porosity	Light to heavy soiling, growth of crusts,	Little, deposits often removable without permanent damage
Sandstone (with partial carbonate cement)	Ashlar, some paving, statuary	Siliceous and carbonate-bearing, low to high porosity	Light to heavy soiling, growth of crusts, scaling of surface and relatively easy loosening of grains	Rapid loss of material, damage often hidden behind a harder soil crust
Limestone	Ashlar, some cladding, statuary	Carbonate-rich, medium to high porosity	Light to heavy soiling, possible rapid growth of crusts and some surface scaling	Loss of material with damage often hidden behind a harder soil crust
Hard limestone	Cladding	Carbonate-rich, low porosity	Light to medium soiling, loss of polish if originally present, long term growth of crusts	Loss of polish by acidic etching, little other permanent damage
Slate	Roofing, some cladding	Siliceous, extremely low porosity	Light soiling	Almost none unless slates are carbonate-bearing when splitting and delamination may occur.

Below. Pollution black soiling of a high-density limestone building in Clacton, Essex.



Is there a cure?

While there are many different building stones available today, historically the use of sandstones and limestones predominated in building construction in the UK since these stones were both commonly occuring and readily available, and easily worked with even primitive tools. Consequently, and unfortunately, most historical buildings within urban areas are at risk.

It is, therefore, appropriate that most conservation efforts involving stone should be directed to sandstones and limestones. In the most dramatic circumstances the laws governing vehicular traffic have been altered in some countries in an attempt to reduce emissions, particularly where there is the potential for photochemical smogs.

However, there are numerous examples where pollution is apparently the result of emissions from a

Return to render

By Alan Gardner, technical secretary of the Society for the Protection of Ancient Buildings

Recently, the Society for the Protection of Ancient Buildings (SPAB) has been asked to comment on very polarised, public and heated debates concerning the (re)application of lime-based external renders to historic buildings.

Lime renders can dramatically change the appearance of a building but may be the best way of limiting further decay.

Since antiquity builders have applied lime-based renders for both technical and aesthetic purposes to buildings of all sorts.

Many building stones decay more quickly if they are exposed to external weathering conditions. Builders in the past would have been aware of this and would have applied renders and / or limewashes to protect the walling. The re-application of a protective external render today can limit the extent of walling replacement necessary and slow down the rate of decay of remaining walling.

It is generally considered good practice to apply limewash to external lime renders to provide protection and prolong the life of the render. The majority of speakers at a SPAB Technical Day in 1997 confirmed this belief.

The importance of lime renders and washes relates to the concept of the porous, 'breathing' building. This is the idea that construction relies on the ability of a structure to encourage the evaporation of moisture which has been absorbed by porous fabric.

Modern construction technology, as a generality, is a fundamentally different concept, relying on impervious outer layers of a system of thin-section barriers to prevent moisture penetrating the fabric.

The introduction and / or failure of impervious materials like cement renders in older buildings and / or disturbance of the traditional performance of the fabric can cause or exacerbate decay in stone, timber or plaster by trapping moisture and preventing evaporation from the walls.

The re-application of a lime render and limewash is technically beneficial to the performance of a tradionally constructed building, which is usually the main reason for proposals to reinstate them.

However, rendering can also be argued for on aesthetic grounds – renders can create a unified whole in terms of the architecture of a building.

Many buildings have been handed down to us having lost their external skins to reveal the bones and muscle beneath. This could either be because of neglect, or due to active removal such as occurred widely during the Victorian period of church restorations.

Indeed, in its early days the SPAB (it was founded in 1877) was given the nickname of 'anti-scrape' because of its opposition to the removal of renders and internal plasters to reveal features beneath.

Much of today's opposition to external re-rendering is based on a reluctance to change the familiar. But this only helps to reinforce the misconception that many of our historic buildings were constructed with walling, especially stonework, left exposed.

The opposition is often further reinforced because the aesthetic of a homogenous Portland cement type of render with modern masonry paint finish is seen as being the

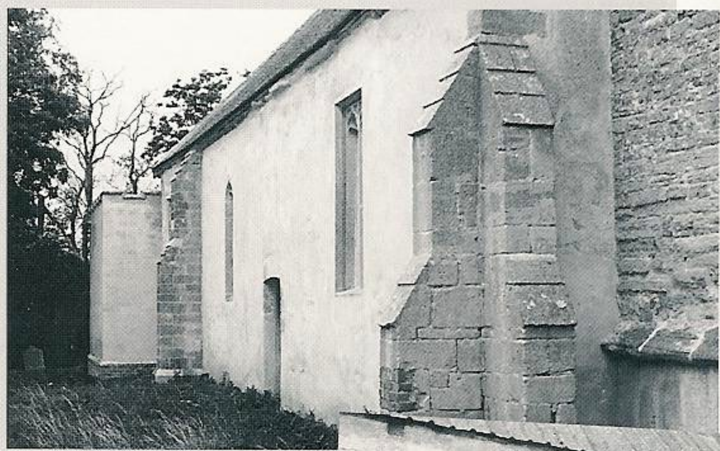


Photo: Tim Ratcliffe

Photo: Andrew Townsend

Lime rendering and washing is not without its opponents but it can be beneficial to the stonework and is often how the building would originally have been finished. The building re-rendered here is Strensham Church, Worcester.

consequence of re-rendering. Lime renders and washes provide a completely different aesthetic to modern materials.

It should be acknowledged that the re-application of a lost lime render can, in philosophical terms, be considered a restoration.

The SPAB usually maintains a presumption against restorations which affect historic character. However, because of the technical and, to a lesser extent, aesthetic arguments, the Society has been supportive of the re-application of protective renders in appropriate lime-based materials on various buildings where this has seemed the best solution to a technical problem.

It could also be claimed, especially where a render has been lost through neglect, that reinstatement can legitimately be called a repair, because the intent is to respond to a technical defect.

This argument is reinforced if it is anticipated that protective lime-based renders will be subject to sacrificial decay.

The Society feels that the best way to conserve buildings is by work which is as limited as possible, but which aims to protect existing fabric in the long term.

The re-application of lime renders is only one of many options on a repairing palette that might achieve these aims.

Local opposition to re-rendering and limewashing proposals is generally based on a commendable wish to protect the perceived original character of a building.

The SPAB is not stating that all historic buildings should be rendered, just that renders can be traditional and are a potentially valuable means of conserving certain old buildings for the future.

● Alan Gardner, SPAB's technical secretary, would welcome any contributions to the debate on the re-application of lime renders and limewashing. Write to: SPAB, 37 Spital Square, London E1 6DY.

neighbouring country, making such legislation apparently irrelevant. Nevertheless, each small piece of action goes some way to making the global total of emissions less than it would otherwise have been and over the past decade total emissions from the UK have begun to fall.

There is still no universally accepted method of dealing with stone decay resulting from air pollution. Every stone in every situation must be individually assessed.

Surface treatments can be exceptionally expensive and the success of a treatment on one kind of stone does not assure its efficacy with another.

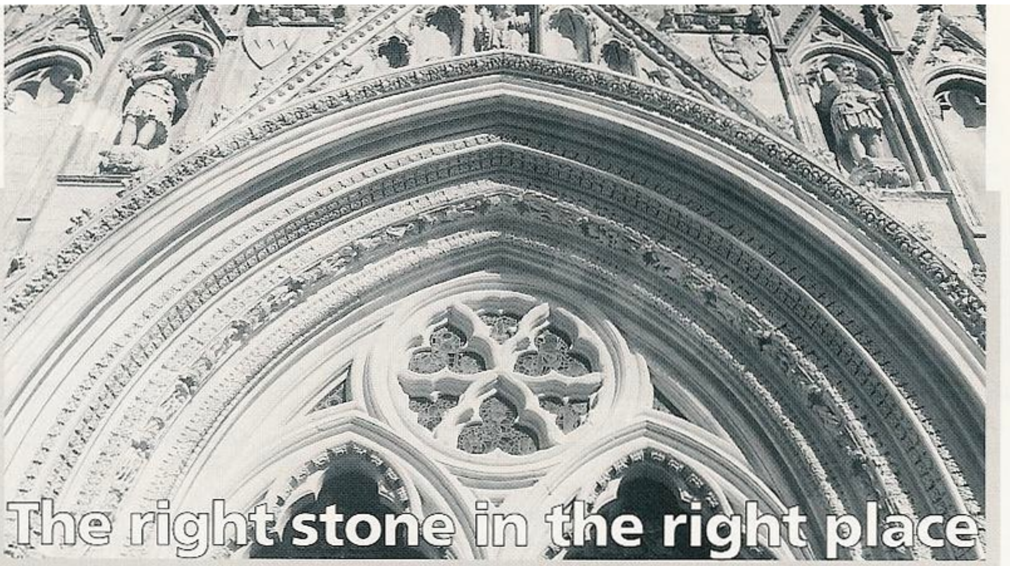
Further, treatments which prevent or restrict the ingress of pollutants in liquid or gas forms may also create a detrimental barrier to the escape of moisture, salts and other media from within the stone. In some instances a treatment may accelerate decay, in the worst scenario even leading to the premature loss of the whole surface.

Unless there is a dramatic change in environmental policy across the globe, we have to accept that all materials are liable to decay in service partly in response to pollution. Stone is no exception.

But if we cannot be sure that our efforts will benefit the stone, is conservation worth the risk? Or do we accept restoration – the replacement of damaged stone, like for like – as being the only viable alternative? There are no easy answers.

The pollution problem does not appear to be a great issue with modern building planners as most have short design lives and expect to be re-fitted, sometimes even within a decade. Furthermore, some prestigious modern cladding systems employ granites and similar hard, low porosity stones that are best able to resist pollution.

Stone in new-build is, though, being used in more ➪



The right stone in the right place

By Ged Smith of Ibstock Building Products

One of the delights of travelling the more rural byways of the UK is noting the local, or vernacular, architecture and relating it to the countryside where it is found. Building materials were heavy and bulky so, unless they were irreplaceable or the developer was wealthy, our forebears did not transport them long distances.

Thus the architecture of London, the Midlands plains and East Anglia are historically brick from local clay deposits (apart from the mansions of wealthy landowners and prestigious buildings in areas such as the City of London).

Where stone was readily available, it was used. And in such a geologically diverse island as ours, a rich variety of stone, too. The honey-coloured Cotswold limestones immediately spring to mind, the gritty sandstones of Yorkshire, the pink granites of Aberdeen and the various-coloured slates of Wales show what lies under the green turf.

An unfortunate by-product of our industrial heritage and damp climate is that much of our stone has been eroded by high levels of pollution for 150 years or more. This is not just a problem associated with the internal combustion engine. Coking gasworks were introduced in the late 19th century and could be every bit as damaging to buildings down wind.

The ill-advised juxtaposition of several different materials on a building, such as limestone cills on a sandstone wall – favoured particularly by the Victorians – accelerated these problems as rainwash from the limestones reacts with the sandstone.

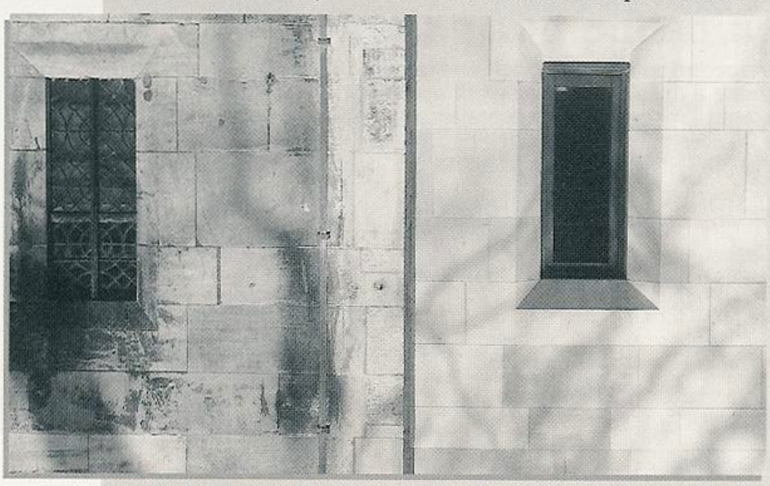
When replacing or refurbishing stone, especially on buildings of national importance, it is important that the new stone weathers to the same appearance as the old. To achieve that, it is necessary to use natural stone as close to the original as possible. A recent example is the refurbishment and extension to the library at York Minster.

This is one of the most important medieval buildings in England, and the work on it was carried out using smooth grained Cadeby magnesian limestone from South Yorkshire. The $500m^2$ extension is finished in dressed ashlar and all additional components, including plinth, string courses, cills and copings, are also in Cadeby.

The masonry and carving work for the extension and refurbishment of the original building was carried out by Cadeby suppliers Ibstock (who also sell bricks and reconstituted stone). Fixing was the work of William Birch & Sons, the main contractors on the project.

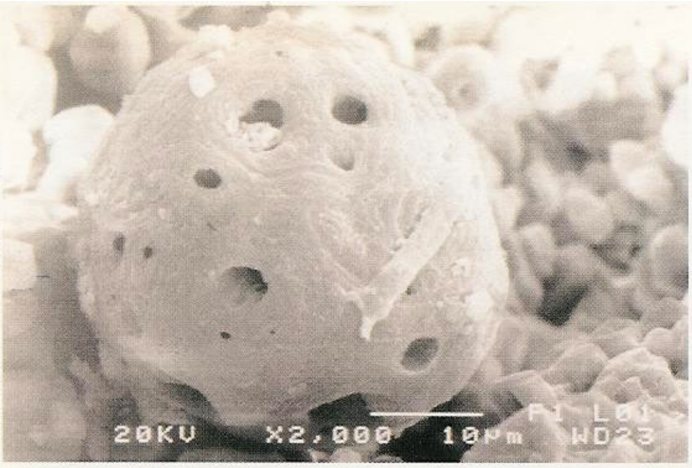
The new extension butts onto the 13th century former chapel of the Archbishops of York, itself built of magnesian limestone, which has served as the Minster library since the early 19th Century.

The extended building occupies a prominent position in the Minster and the importance of the quality of its appearance cannot be underestimated. By using local limestone, the extension will soon blend with the adjoining 700-year-old building.



Above. The original, 700-year-old building of York Minster and the new extension. The difference is stark now, but the new Cadeby limestone will quickly weather to match the older stonework.

Top. As well as the extension, the original building of York Minster was refurbished, the stone being replaced where necessary with Cadeby magnesian limestone from Ibstock Building Products.



With permission of Dr R M Esbert and Mr F Díaz-Pache

A Scanning Electron Microscope image of a pollution particle present within limestone black crust at the Cathedral of Burgos, Spain.

experimental ways. An increasingly wider selection of stones is being employed in ever more diverse and critical locations. Also, architects are now specifying that the stone should remain pristine for the duration of the design life.

Recognising the threat of pollution damage and dealing with it appropriately will enable a wide range of stones to be used with confidence providing there is good selection of both the stone and possible effective protective treatments.

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