

**PORE PROPERTIES AS INDICATORS OF BREAKDOWN MECHANISMS IN
EXPERIMENTALLY WEATHERED LIMESTONES**

Dawn T. Nicholson

School of Earth Sciences, University of Leeds, LEEDS LS2 9JT, UK.

Tel: 0113 233 5234 Fax: 0113 233 5259 e-mail: dawn@earth.leeds.ac.uk

Short title: Pore properties as indicators of rock breakdown

ABSTRACT

The results are reported of four experimental weathering tests: freeze-thaw, wetting and drying, slake durability and salt weathering, on five different types of limestone. Effective porosity, mercury intrusion porosimetry and SEM were used to evaluate changes in pore properties, while weight loss and fracture density were used to assess deterioration severity. A primary aim was to observe modifications in porosity due to weathering and to draw inferences about the internal rock deterioration mechanisms taking place.

It is concluded that the five limestones not only show a wide range of resistance to weathering in general but considerable difference in resistance to particular weathering processes. Consequently, when assessing durability it is essential to consider rock properties in the context of the weathering process to which the rock is subject. The type of deterioration indicator used is also important in interpretation of durability.

A variety of pore modification mechanisms operate, including changes in pore connectivity, pore infilling, and the introduction of additional void space. There are indications that changes to the internal pore structure of rocks due to weathering may be a pre-cursor to more substantial macro-deterioration.

Keywords: Porosity, limestone, weathering, breakdown mechanisms, durability

INTRODUCTION

Experimental studies have shown that porosity and pore size distribution influence rock susceptibility to weathering (Winslow and Lovell, 1981; McGreevy, 1996; Ordonez *et al.*, 1997). The precise role of these and other pore properties, however, has not been precisely determined because there is no single controlling property, but rather a combination of properties (Matsuoka, 1990). Indeed, interactions between mechanical, lithological and pore properties of rocks and the nature of the weathering processes affecting them create a complex system. In this paper, data are presented in which modifications to pore properties resulting from experimental weathering of five contrasting limestones are examined. Despite an ever-growing literature covering changes to mechanical properties (e.g. sonic velocity and elasticity) due to weathering (e.g. Allison, 1988; 1990; Goudie, *et al.*, 1992; Allison and Goudie, 1994; Remy *et al.*, 1994; Murphy and Inkpen, 1996; Allison and Bristow, 1999), there are comparatively few studies that focus on changes to porosity and other void-dependent properties such as pore size distribution, degree of saturation and water absorption capacity. McGreevy (1982), for example, reports an increasing degree of saturation with time of immersion and Bland and Rolls (1998) refer to experimental work (no reference cited) in which repeated wetting and drying resulted in increased sample saturation coefficient, and increases in the size of pores and microcracks. Whalley *et al.*, (1982) also make reference to the phenomenon of changing capillarity within a rock fracture as weathering proceeds. However, there are relatively few experimental data presented in the literature which support and verify these assertions (e.g. Brockie, 1972; Accardo

et al., 1981; Fitzner, 1988; Tugrul, 1997; Pombo-Fernandez, 1999). In an attempt to remedy this deficit, this study aims to;

- (i) measure modifications to porosity resulting from experimental weathering of several limestones;
- (ii) determine what these modifications infer about the internal rock breakdown mechanisms taking place; and
- (iii) identify any correlation between modification of porosity and rock deterioration.

To provide a contextual basis, the relative resistance of the limestones to different experimental weathering conditions is first determined and the relative severity of the tests described.

SAMPLE CHARACTERISTICS

Five limestone types ranging from Carboniferous to Cretaceous in age were used in this study (Table 1). Four of the samples were cut from loose blocks lying in disused quarries or in old road cuttings and one was cut from a recently engineered road cutting (MagL). The limestones have a wide range of properties, with effective porosity (n_e) ranging from less than 1% to 33%, compressive strength varying from 7 to 80MPa, and P-wave velocity varying from 1970 to 6240ms⁻¹. A wide range of responses to experimental weathering was therefore expected. Further details of these and other rock properties are given in Table 2.

SEM observations show that SpaL (Figure 1a) is a dense, sparry limestone with some interlocking of blocky and detrital grains. Pore spaces are usually $<2\mu\text{m}$ and commonly a fraction of this size. It is notable that larger pores are found in association with fossil fragments. In the oolitic limestone (OoL) (Figure 1b), the concentric shells of ooids are densely packed, but there are very large ($>30\mu\text{m}$) macro-pore spaces between these concentric layers. The high density chalk (HdCh) (equivalent to 'very hard' chalk as defined by Mortimore and Fielding 1990) shows some grain interlocking and many pores in the range 0.5 to $2\mu\text{m}$, with higher porosity in the vicinity of coccoliths (Figure 1c). The magnesian limestone (MagL) shows moderate grain interlocking and a predominance of coarse pores in the range 30 to $100\mu\text{m}$ (Figure 1d), often connected by extremely narrow pore throats with potential for coalescence (Figure 1e) and microcracks of 2- $3\mu\text{m}$ in width. Small cracks also occur at the boundary of pores. The low density chalk (LdCh) (equivalent to 'soft' chalk as defined by Mortimore and Fielding 1990) is extremely porous with the pores usually being well-defined (Figure 1f).

EXPERIMENTAL PROCEDURE

Four weathering tests were conducted; freeze-thaw, wetting and drying, salt weathering and slake durability. Each was interrupted on several occasions to allow for repeated measurement of weight loss, fracture density (not measured for slake durability due to specimen geometry), effective porosity and dry density on each specimen. These measurements were also collected before

and after weathering testing. Pre- and post-test mercury intrusion porosimetry data were also collected (for the freeze-thaw and salt weathering tests only) and details of measurement are given below. Specimens for all tests except slake durability were a standard cylindrical shape of dimensions 50mm diameter by 100mm length to reduce the potential effect on results of variations in size and shape (Goudie, 1974).

Freeze thaw test method

Five to nine specimens per sample were subjected to repeated cycles of freeze-thaw in a modified domestic chest freezer with a built-in heat source. Specimens were saturated at the start of the experiment and were set upright in a bath of distilled water with a depth of 30mm. Each freeze-thaw cycle lasted 24 hours, comprising 18 hours of freezing to $-18\pm 2^{\circ}\text{C}$ at a mean rate of 2°C/hr , and 6 hours of thawing to $+18\pm 2^{\circ}\text{C}$ at a mean rate of 6°C/hr . The timing of test interruptions varied for each rock and was based on a pre-test estimate of behaviour under experimental weathering and also from regular inspections of specimens during testing to monitor change qualitatively.

Salt weathering test method

The experimental method adopted was broadly based on ASTM C88-90 (1990) and D5240-92 (1992), which together describe the method for magnesium sulphate soundness testing of rock. Oven-dried specimens were placed in individual mesh bags and completely immersed in a saturated solution of magnesium sulphate for a period of 16 to 18 hours. The solution was

maintained at a temperature of 20 to 22°C throughout testing. Following this immersion period, specimens were removed from the solution, permitted to drain for 15 minutes, carefully removed from the mesh bags and placed on metal trays in the drying oven (pre-heated to 105±2°C). Specimens were dried until constant weight was achieved. To repeat the cycle, oven-dried specimens were cooled at room temperature before being replaced in the mesh bags and re-immersed. There was no attempt throughout testing to control humidity conditions. For each sample five specimens were used and the test procedure was repeated for five cycles. The test was interrupted after one cycle and again after three cycles, with the exception of HdCh, which was just interrupted after two cycles. At each interruption and at the end of testing, specimens were washed to remove sulphate solution. The reaction of wash water to a solution of barium chloride (BaCl₂) was used to indicate successful removal of sulphate solution, however, weight loss and porosity data indicate that removal of internal salts may not have been complete.

Wetting and drying test method

The wetting and drying test was set up in accordance with ASTM D5313-92 (1992). Specimens were placed on a 6mm layer of coarse sand and dried beneath a single 150W infra-red lamp positioned 450mm above the samples. Following drying for at least 6 hours (maximum 10 hours) specimens were removed from the drying tray, cooled at room temperature and then immersed in water for at least 12 hours. Just two (LdCh and HdCh) of the five samples were tested, with five specimens being used for each. LdCh was subjected to

80 cycles (interrupted after 10, 25 and 50 cycles), while 40 cycles were used for HdCh (interrupted after 4, 12 and 24 cycles).

Slake durability test method

For each sample, ten 30mm cubes were subjected to a standard slake durability test following the requirements of Franklin and Chandra (1972), with the exception that five cycles were used instead of the usual two. The test provides an index of susceptibility to slaking and abrasion by subjecting specimens to repeated 10 minute cycles of rotation in a wire mesh drum partially immersed in water. For each test, ten test pieces are rotated simultaneously. In between each rotation cycle, specimens were dried at $105\pm 2^{\circ}\text{C}$ to constant weight and a dry weight obtained.

ASSESSMENT OF DURABILITY

Weight loss

Weight loss is usually calculated on the basis of a retained portion represented by the mass of the largest remaining piece following testing. However, this can be very misleading, particularly if a specimen breaks into two or three pieces of similar size. Weight loss, and consequently rock durability is then grossly over-estimated. A modified weight loss criterion is therefore used here where all fragments exceeding 10% of the initial specimen dry mass contribute to the retained portion. Similar, though not identical criteria, have been adopted in

other rock weathering studies (Goudie 1974, 1999; Williams and Robinson, 1998). Measurements were made to a mean accuracy of $\pm 0.1\%$.

However, the use of weight loss as the sole indicator of deterioration in many weathering experiments has limitations because it only reflects the extent of material detachment. It does not measure *in situ* deterioration (e.g. fracturing) or deterioration which is not visible in hand specimen. To overcome the over-reliance on a single indicator, a second parameter known as 'Fracture Density' is also used in this study.

Fracture density (F_D)

Fracture density is a measure of the total surface area of fractures (mm^2) per unit volume of rock (mm^3) and reflects *in situ* deterioration. Fracture density assumes that fractures are obloid in three-dimensional form (penny shaped in plan and elliptical in cross-section) and is determined from the relationship $2P_L$, where P_L is the number of point intersections (P) of fractures per unit length (L) of grid line (Underwood, 1970). P_L is normally obtained by point counting of intersections on gridlines drawn on a *section plane* through the medium. However, the method has been modified here, to suit the cylindrical form of specimens used and to enable non-destructive monitoring throughout experimental weathering. A standard grid was superimposed on the surface of each specimen (Figure 2). The number of point intersections (P) of all fractures visible to the naked eye was counted and the total gridlength (L) measured with

a calliper to an accuracy of 0.01mm. Fracture density was measured before, during and after weathering tests.

Saturation porosity

Effective porosity (n_e) and dry density (ρ_e), measured to a mean accuracy of $\pm 0.5\%$, were determined using the 'displacement method' (Brown, 1981), a procedure which involves free saturation of rock at ambient pressure and therefore often does not reflect maximum effective porosity. Pre-test values of n_e for individual specimens are given in Table 2. Pre- and post-test measurement conditions were identical, including drying regime, to limit the influence of moisture retention in pore spaces.

Mercury intrusion porosimetry

Mercury intrusion porosimetry is based on capillary law, which states that intrusion into pores of a non-wetting liquid such as mercury, depends upon the amount of pressure applied to that liquid. When such pressure is applied, the amount of intrusion which results at any given pressure is related to the diameter of pore throats as determined by the 'Washburn Equation' (Washburn, 1921):

$$D = \frac{-4\gamma \cos \theta}{P} \times 10^6 \quad [1]$$

Where D = pore throat diameter (μm), P = applied pressure of intruding mercury (N/m^2), γ = surface tension (N/m), and θ = contact angle. As pressure is

increased, mercury intrudes into pores of smaller diameter. Mercury porosimetry was undertaken on oven-dried specimens using an Autopore II 9220 porosimeter, capable of delivering a maximum pressure of 414MPa (60,000psi) and of measuring pore throat diameters ranging from 0.0036 μ m to 100 μ m. Experimental results are based on the assumption of cylindrical pores, with a standard contact angle of 140° and a mercury surface tension of 485d/cm. Porosity measured using mercury impregnation (n_m) usually gives a value which is greater than n_e but less than total porosity (n_t).

Because it is not possible to conduct pre- and post-test mercury porosity measurements on the same test specimen considerable caution is needed in the interpretation of this data. Prior to conducting the experimental weathering tests mercury porosimetry was undertaken on a single specimen of rock considered to be representative of each limestone type on the basis of visual estimation and comparison of n_e with values for the main sample (refer to Tables 2 and 3). At the end of testing a further set of mercury porosimetry data was obtained for each limestone type based on a single sub-specimen cut from one of the main test cylinders. Pre- and post-test mercury porosimetry data are given in Table 3 and pore size distributions for the limestones are shown in Figure 3. Because of the test procedures used it is recognised that variability between specimens might explain some of the difference between pre and post-test measurements and hence they are unreliable if used as the sole source of interpretation. Nevertheless, reference is made to the general trends apparent

from mercury porosity data where they shed light on interpretations made on the basis of the more reliable n_e data.

RESULTS I: DETERIORATION INDUCED BY EXPERIMENTAL WEATHERING

Weight loss and change in fracture density

As expected, weight loss (Figure 4) and changes in fracture density (Figure 5) were variable. Mean sample weight loss and fracture density data are given in Table 4. All samples showed weight loss and an increase in fracture density after freeze-thaw testing, with extremely low resistance exhibited by OoL and LdCh, both of which rapidly disintegrated. Following salt weathering, some samples showed a net weight gain (OoL and HdCh) despite, in the case of OoL, minor granular loss. OoL was much more resistant to salt weathering than to freeze-thaw, but LdCh again exhibited rapid and extensive deterioration. Both samples tested for wetting and drying (LdCh and HdCh) were extremely resistant. Sample SpaL exhibited the greatest resistance to slaking while sample LdCh was least resistant. There was generally a good correlation between fracture density and corresponding weight loss, with the exception of HdCh following salt weathering, which suffered little change in weight but developed intense incipient fracturing.

Rock susceptibility to weathering

The ranking of each sample for weight loss and change (Δ) in fracture density due to freeze-thaw was:

Weight loss: OoIL > LdCh > HdCh > MagL > SpaL

Δ Fracture density: OoIL > LdCh > HdCh > MagL > SpaL

The ranking for salt weathering was:

Weight change: LdCh(+) > MagL(+) > HdCh(-) > OoIL(-) > SpaL(0)

Δ Fracture density: LdCh > HdCh > MagL > OoIL > SpaL

For wetting and drying, LdCh was less slightly resistant than HdCh.

The ranking for slaking was:

Weight loss: LdCh > OoIL > MagL > HdCh > SpaL

For each test where weight loss and fracture density was measured, there was a close correlation in the ranking of samples. This suggests that use of a single deterioration indicator may be sufficient where a crude, relative measure of durability is required.

For the freeze-thaw and salt weathering tests it is apparent that although the most resistant rock, SpaL, was always the most resistant, the resistance of the other samples varied. Increasing susceptibility to salt weathering correlated reasonably well with a decrease in microporosity (μm) (data given in Table 3) with the exception of SpaL and an increase in total connected pore volume (n_e), the latter being similar to the findings of McGreevy (1996). The high microporosity of OoIL may explain its much greater resistance to salt

weathering than to freeze-thaw, since salt solution might not enter smaller pores with the same ease as water (Fitzner, 1988). There was no clear relationship between susceptibility to freeze-thaw and pore properties for the samples tested in this study. These results indicate that durability should never be considered in isolation, but with reference to the relevant weathering test and/or environmental conditions.

Relative severity of experimental weathering tests

If the weathering tests are ranked with respect to weight loss and fracture density, an indication of their relative severity can be obtained:

	<i>For weight loss*</i>	<i>For fracture density</i>
LdCh:	FT > MS > SD > WD	MS > FT > WD
MagL:	FT > MS > SD	MS > FT
OolL:	FT > SD > MS	FT > MS
HdCh:	FT > MS > SD > WD	MS > FT > WD
SpaL:	SD > FT > MS	MS > FT

* Using weight *change* for salt weathering, and the inverse of weight loss for slake durability
 FT = freeze-thaw; MS = salt weathering; SD = slake durability; WD = wetting and drying

This ranking suggests that freeze-thaw is more likely to result in the detachment of rock fragments, leading to weight loss, whereas salt weathering is more likely to lead to incipient fracturing. This result may, in part, reflect the binding effect of salt (Booth, 1990) but that is unlikely to account for all of this trend. It was notable that much of the binding effect of salt was lost when samples were re-immersed, or at the end of testing when they were washed. It can therefore be

presumed that any incipient fractures remaining after immersion or washing procedures represent genuine incipient fractures, i.e. mechanical breaks with some tensile strength, and are not merely open cracks held together temporarily by re-crystallised salt. For OoL, freeze-thaw resulted in much more deterioration both in terms of fragmentation and incipient fracturing, than was the case for salt weathering. This suggests that for comparison of results across different tests more than one deterioration indicator should be used to describe durability. An ideal solution would be to utilise a range of indicators, including the non-destructive methods used here, plus, for instance, change in elasticity (Allison, 1988, 1990) and sonic velocity (Matsuoka, 1990), and perhaps pre- and post-test comparisons using destructive methods such as the micropetrographic index (Irfan and Dearman, 1978).

From the above ranking, wetting and drying, and slaking, are least likely to cause deterioration for the range of rocks tested. Apparently, SpaL is an exception to this observation, but this can be explained by the fact that this limestone was generally extremely resistant to deterioration.

RESULTS II: POROSITY MODIFICATION

Percentage change in effective porosity for individual specimens for each weathering test is shown in Figures 6 to 9. Absolute pre- and post-test values are summarised in Table 5. The results show that both increases and decreases in n_e occurred, with some samples exhibiting no significant change.

There are several reasons why increases in porosity can occur due to weathering.

Micro-cracking: This involves either initiation and propagation of new cracks or the extension and widening of existing cracks. Microcracks may initiate at flaws and heterogeneities in rock (Kranz, 1983) and internal fluid pressures such as those which may be induced by the freeze-thaw and salt weathering processes are particularly effective in producing crack growth (Pollard and Aydin, 1988; La Iglesia *et al.*, 1997). Studies have also shown that chemical processes can lead to stress corrosion in which cracks develop where mechanical stresses are less than the critical stress intensity (Whalley *et al.*, 1982; Atkinson and Meredith, 1987; Mottershead and Pye, 1994). Microcracks can develop independently, or can link existing microcracks or pores.

Pore enlargement: Loose debris contained in pore spaces, perhaps generated by the break up of grain contacts (Fitzner, 1988), might be flushed away from pore throats in the saturating medium and out of the rock. If this debris is merely re-distributed within the pore structure then although connectivity could be improved there would be no net change in total pore volume. For the level of weighing accuracy used in this study, removal of loose debris would be unlikely to be detected in weight loss assessment. An alternate way in which pore enlargement could occur is through compression of pore walls due to internal growth of ice or salt crystals. This may only be effective in less resistant rocks.

Dissolution: Dissolution certainly has the potential to affect the limestones tested here. However, it is uncertain whether the mechanism could be effective over the short-term period of these experiments, although significant modification of limestones during short-term exposure trials has been measured (Moses and Viles, pers. comm.) suggesting that it could.

Surface adhesion: Brockie (1972) suggested that 'roughening' of rock surface texture due to shedding of fine particles from rocks during freeze-thaw could increase n_e since more water could be retained by adhesion at the surface.

There are also several mechanisms that can bring about a reduction in total pore volume and these include:

Curing: Lienhart and Stransky (1981) found that rocks were more likely to resist experimental freeze-thaw if they had undergone several cycles of pre-test wetting and drying. They described this phenomenon as 'curing'. They proposed that one of the ways that curing could work was by case hardening due to leaching of internal cementing agents and their deposition onto specimen surfaces. This would render rock less permeable and hence reduce saturation efficiency, although total pore volume may be unaffected.

Deposition of crystallised salts in pores: The uptake of salts and the 'binding' effect which sometimes results is a well-known phenomenon (Booth, 1990; Goudie, 1974; McGreevy, 1996; Williams and Robinson, 1998). Pore infilling

appears to occur for many of the rocks tested here and explains why some of these also showed weight gains.

Pore compression: Collapse or compression of pores may also occur, particularly in less resistant rocks. This may occur under extreme conditions as a result of, for example, the pressure of ice exerted on the rock surface.

Post freeze-thaw (Figures 6a to 6e)

Freeze-thaw produced an increase in mean sample n_e of 1% for MagL. The absence of any corresponding change in density (Table 5) indicates that there was no change in total pore volume, but that the increase in n_e represents improved saturation due to modification of existing pores. This might have been achieved by the flushing away of loose debris from around pore throats. There is also some evidence of pore coalescence and linking of microcracks from SEM analysis (Figure 7a). For MagL there was much greater consistency between individual specimens than for other limestone types (Figure 6b). However, MagL also showed considerable fluctuation in porosity, with a sharp increase at 32 cycles being followed by a significant decrease by the end of testing. These temporal fluctuations are matched by sonic velocity data (not presented here) and are difficult to explain.

HdCh responded similarly to MagL (Figure 6d) and showed the largest absolute increase (3%) in n_e . There was also an absence of change in density (Table 5) indicating improved saturation, and trends between specimens were consistent,

though not as clearly defined as those for MagL. It is notable that the steepening of the curve of n_e against time at the end of testing indicates a progressive modification.

LdCh showed an overall reduction in n_e of more than 2% and a small, corresponding increase in density but there was considerable variability between specimens (Figure 6a). An increase in density seems to suggest that compression of the sample has taken place. Data obtained from mercury porosimetry also indicate a reduction in porosity (n_m) as well as a reduction in modal pore size and a significant increase in μ_m . If the trends indicated by both sets of data are real, this suggests either that throat blockage has occurred, perhaps by debris re-distribution, or that pores have been compacted in some way. Case hardening of the type described by Lienhart and Stransky (1981) could be responsible for the reduction in n_m shown in LdCh but would not explain the increase in finer pores.

Mean change in n_e for OoL and SpaL at the end of testing was negligible or insignificant though in the former case there was considerable variation between specimens. Examination of weight loss data for individual specimens of OoL (Figure 6c) shows that specimens which were initially more resistant to deterioration showed a significant (3%) increase in n_e and corresponding reduction in density. This suggests that the increase in n_e reflects the generation of new void space in the rock and not merely more effective saturation. It is not clear whether this means that increased porosity represents

some form of 'curing', temporarily increasing durability, or simply whether introduction of new void space occurs prior to macro-scale deterioration.

Post salt weathering (Figures 8a to 8e)

All of the limestones showed an absolute decrease in n_e (Figures 8a to 8e) by around 0.5% in OoL and SpaL, 2-3% in MagL and HdCh, and 6% in LdCh. This is probably due to retention in pore spaces of crystallised salts and this would account for the weight gain measured for some of these rocks and the increases in density (Table 5). Unusually, in MagL, all specimens showed an initial increase in n_e , followed by a subsequent reduction (Figure 8b). This might indicate that modification of the pore structure was necessary before salt solution was able to gain access to finer pores.

A reversal of the decreasing porosity trends exhibited by some rock samples (e.g. OoL and HdCh) became evident in the latter stages of the test. The rate at which porosity modification occurs differs in different rock types, with some clearly responding much more rapidly. Despite the strong indications of porosity reductions in LdCh and MagL, SEM evidence of pore infilling is difficult to detect. A fine coating of salt deposits on and between grains is evident in micrographs for OoL (Figure 7b).

With the exception of LdCh, post-test mercury porosimetry measurements showed an increased porosity, in contrast to the changes exhibited by MagL,

OoL and HdCh as determined by the saturation method. This difference may be the result of several factors such as;

- scale effects resulting from the difference in size and shape between cylindrical test specimens and the small (3cm³) cubes used in mercury porosimetry,
- between specimen variability,
- improved fluid saturation under high pressure of pores partially infilled with salt.

Nevertheless, pre- and post-test n_m trends for MagL and HdCh are probably reasonably reliable and suggest that in addition to pore infilling, salt weathering induced new void space into the rocks. SEM analysis shows, for example, many new cracks in HdCh at all scales (Figures 7c, d and e). As well as microcracks with an aperture of around 1 μ m (Figure 7c) there were also larger scale fractures, visible in hand specimen (Figures 7d and e). Other studies (e.g. Fitzner, 1988; Ordonez *et al.*, 1997) indicate that the initial deposition and growth of salts and ice crystals first occurs in large pores. Once these are filled further growth continues into smaller diameter pores. MagL has a notably higher proportion of coarse pores than the other limestones (Figures 3 and 7f) and it is possible that salt did not enter many of the finer pores since the coarse pores had not been completely filled.

Post wetting and drying (Figures 9a and 9b)

Only two samples were tested for wetting and drying. HdCh (Figure 9b) showed an increase in n_e while LdCh (Figure 9a) showed a small reduction. While HdCh

showed very strong consistency between specimens and little temporal variation, LdCh was much more variable. The absolute increase in n_e for HdCh of 3.5% was bigger than the change for this sample under any other test. This is surprising since this rock did not indicate any larger-scale changes under these test conditions. For the wetting and drying test there was no significant change in ρ for HdCh indicating that in both cases the change in n_e reflects changes in the degree of saturation achieved. The break up of grain contacts and flushing out of loose debris from pore throats might be responsible for this apparent increase in n_e .

Post slake durability (Figures 10a to 10e)

Following slake durability testing HdCh showed a reduction in n_e while the remaining limestones showed no significant change. For all samples there was close correspondence between individual specimens (Figures 10a to e). Like the wetting and drying test, the lack of change in ρ for HdCh indicates a change in the saturation efficiency of the limestone, though in this case a reduction. This may have been brought about by the case hardening process described above.

RELATIONSHIP BETWEEN PORE RESPONSE AND DETERIORATION

The basic hypothesis of this work is that rock breakdown by fracturing and fragmentation will be preceded by modification at the micro-scale, including microcracking, pore coalescence and enlargement both of which contribute to

the generation of macrofractures and large-scale fragmentation. In granular rocks, grain boundary microcracks (Simmons and Richter, 1976) can lead directly to disintegration (Nicholson and Nicholson, 2000) and this has been seen to a limited extent in OoL. In non-granular rocks, however, microcrack linking and coalescence can give rise to macrofractures that are visible at the rock surface. If sufficiently persistent, these in turn give rise to detachment and fragmentation. Pores can also contribute to this process by enlargement and coalescence. It is reasonable to expect, therefore, that macro-scale evidence of deterioration would be reflected in micro-scale modifications of the type described above. In the next section, therefore, the role of porosity modification in rock deterioration is explored. For convenience, rocks are grouped with respect to their deterioration response.

Samples exhibiting significant deterioration

Macro-scale deterioration corresponded with evidence of increased porosity in MagL, OoL and HdCh after freeze-thaw testing and with generation of new voids in MagL and HdCh after the salt weathering test. LdCh, which also deteriorated severely after freeze-thaw, is discussed separately below.

Although some of the limestones followed similar trends they differed markedly in terms of the absolute amount of deterioration involved, especially for the freeze-thaw test. For example, HdCh experienced almost four times the weight loss experienced by MagL, yet both were characterised by an increase in n_e indicating improved connectivity. These differences could reflect the influence of

other textural and lithological controls. Furthermore, the fact that the total pore volume of MagL is much higher than that of OoIL and that its saturation coefficient is much lower (0.56 for MagL compared with 0.99 for OoIL), may suggest a greater capacity to take up the pressure of ice crystallisation. Alternatively, this could be explained by structural differences with MagL displaying a partially interlocked crystalline structure compared to the relatively weakly cemented OoIL.

Most of the rocks which experienced deterioration due to salt weathering also experienced pore infilling leading to a *reduction* in porosity and making it difficult to detect *increases* in porosity caused by deterioration. Nevertheless, increases in porosity were sufficiently great in some cases (eg MagL and HdCh) to be detected.

Rocks in which it could be inferred that new void space was generated are also those which suffered the most intense deterioration due to weathering (e.g. OoIL after freeze-thaw; HdCh after salt weathering), though LdCh is anomalous in this respect. Conversely, of the rocks which *did* deteriorate, *least* deterioration occurred in those in which improved connections between pores could be inferred (eg MagL and HdCh after freeze-thaw).

Samples exhibiting minimal deterioration

Samples that largely resisted deterioration would not be expected to show significant changes in pore properties. This was the case for SpaL following

freeze-thaw and salt weathering, LdCh following wetting and drying, and MagL, OoL and SpaL following slaking. The nature of the weathering process involved in slaking is such that breakdown is by surficial abrasion and granular disintegration. As such, it is not expected that significant modifications to pore structure would occur by microcracking, for instance, although pore enlargement by dissolution and improvement to pore connectivity are still possible. Using the empirical approach of Winslow and Lovell (1981), in which the slake durability index is calculated on the basis of a range of pore properties, completely anomalous results are obtained for the rocks tested here. In part, this is an indication that for this group of limestones, slaking cannot be expected to produce changes in pore structure.

Samples which behaved converse to expectations

There are two examples for which observed changes are not in accord with the hypothesis suggested above:

(i) *Low density chalk (LdCh)*

Following freeze-thaw, LdCh showed a significant reduction in n_e . This was not expected, given the severe deterioration exhibited by this rock type. It is possible that given the inherent weakness and high compressibility of LdCh, a reduction of void volume and connectivity may have occurred as a result of compaction or pore collapse. Conversely, after slaking, in which significant rounding of LdCh specimens occurred, no modification of porosity was

recorded. This may reflect the nature of the test in which surface mechanical abrasion and damage is much more important than internal modification.

(ii) *High density chalk (HdCh)*

High density chalk resisted deterioration during wetting and drying and slake tests but data indicate that pore modification did occur. Wetting and drying induced a significant increase in n_e and improved saturation efficiency rather than an increase in total void volume can be inferred. The increase in n_e occurred steadily and progressively from the start of testing without any reciprocal change in ρ . It is unclear whether by the end of testing the observed change in n_e represents a stable condition or whether visible deterioration would have occurred had there been further cycles of wetting and drying. The reduction in n_e after slaking might indicate case hardening or slight compaction of the rock due to impact and abrasion. This seems unlikely, however, since such an effect is absent in other less resistant rocks (e.g. MagL and OoIL). Another possible explanation for the behaviour of HdCh in the slaking test is that near-surface clogging of pores due to fines in suspension in the slaking water could have influenced water absorption at the surface.

Further discussion

Analysis of pore modifications due to weathering indicates that some effects owe more to the nature of test conditions than to breakdown mechanisms *per se* (e.g. pore infilling by salt).

There is some evidence in the results presented here of a link between micro-scale and macro-scale deterioration processes. It is therefore proposed that pore structure modification may be a two-stage process.

Stage 1: Increased pore connectivity by modification of existing pore structure

The first stage in this process is micro-scale pore structure modification which leads to an increase in water absorption but does not result in any change in the total void volume. Less energy expenditure would be involved if internal weathering-related pressures from water migration or crystallisation of ice or salt, for example, could be taken up in existing pore spaces rather than creating new voids. This could be achieved by the breaking up of grain contacts and re-distribution of debris. These mechanisms are likely to modify the pore size distribution and increase connectivity, but are not accompanied by any visible or measurable deterioration at the macro-scale. The response of HdCh to wetting and drying and MagL to freeze-thaw are examples of this behaviour.

Stage 2: Increased total void volume by generation of new void

The second stage involves generation of new voids through microcracking and/or pore coalescence. The response of OoL and HdCh to salt weathering are examples of this behaviour.

It is likely that as internal pore structure modifications progress from stage one to stage two, macro-scale deterioration would become increasingly obvious. The mode and severity of such deterioration might be broadly unrelated to pore

structure however, and as stated before, more dependent upon a range of mechanical, lithological and structural rock properties.

CONCLUSIONS

The different response of limestones to a range of weathering tests indicates that durability should be investigated in the light of the specific weathering conditions involved. A striking finding is the contrast in ranking obtained depending on whether weight loss or fracture density is used as the primary indicator. This contrast also highlights the need to select deterioration indicators with care and is evidence that different macro-scale breakdown mechanisms are involved for frost shattering and for salt weathering, supported by the broad correlation of different pore properties with deterioration for these two tests.

Analyses of pore modifications due to weathering indicate that a variety of mechanisms could be responsible for modifications of pore structure. There are indications that modifications to the existing pore structure precede more substantial rock damage by introduction of new voids through pore coalescence and microcracking. An alternate interpretation is that modification of the existing pore structure leading to increased saturation represents a 'curing' process, which has the effect of rendering rock more durable. Generalisations concerning the mechanisms of deterioration disguise significant differences in its severity.

Measurement and observation of porosity and other properties before, during and after weathering tests is a useful approach which provides additional insights into the mechanisms of modification. Further investigation of a wider range of rock types is needed to more fully assess the nature of processes operating and their influence on rock breakdown.

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REFERENCES

- Accardo G, Rossi-Doria P, Sammuri P, Tabasso M. 1981. Artificial weathering of Carrera Marble: Relationships between the induced variations of some physical properties. *The Conservation of Stone II*. Pre-prints of the contributions to the International Symposium, Bologna, Italy, 243–273.
- Allison R.J. 1988. A non-destructive method of determining rock strength. *Earth Surface Processes and Landforms* **13**, 729–736.
- Allison R.J. 1990. Developments in a non-destructive method of determining rock strength. *Earth Surface Processes and Landforms* **15**, 571–577.
- Allison R.J., Bristow G.E. 1999. The effects of fire on rock weathering: some further considerations of laboratory experimental simulation. *Earth Surface Processes and Landforms* **24**, 707–713.
- Allison R.J., Goudie A.S. 1994. The effects of fire on rock weathering: an experimental study. In Robinson D.A., Williams R.B.G. (eds) *Rock Weathering and Landform Evolution*. J. Wiley & Sons Ltd, Chichester, 41–56.
- American Society For Testing Materials C88. 1990. *Standard Test Method For Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate*, Philadelphia.
- American Society For Testing Materials D5240. 1992. *Standard Test Method For Testing Rock Slabs to Evaluate Soundness of Riprap by Use of Sodium Sulfate or Magnesium Sulfate*, Philadelphia.
- American Society For Testing Materials D5313. 1992. *Standard Test Method For Evaluation of Durability of Rock for Erosion Control Under Wetting and Drying Conditions*, Philadelphia.

Atkinson BK, Meredith PG. 1987. The theory of subcritical crack growth with applications to minerals and rocks. In Atkinson BK, (ed.) *Fracture Mechanics of Rock*. Academic Press, London, 111–166.

Bland W, Rolls D. 1998. *Weathering: An Introduction to the Scientific Principles*. Arnold, London.

Booth AI. 1990. Sandblast erosion tests for the physical characterisation of chalk. In *Chalk*, Thomas Telford, London, 187–194.

Brockie WS. 1972. Experimental frost shattering. *Proceedings of the 7th New Zealand Conference, Conference Series 7*. Hamilton. New Zealand Geographical Society, 177–186.

Brook N. 1990. The disc test. *Leeds University Mining Association*, 49–55.

Brook N. 1993. The measurement and estimation of basic rock strength. In Hudson JA, (ed.) *Comprehensive Rock Engineering Principles, Practice and Projects 3*. Pergamon Press, Oxford, 41–66.

Brown ET. (ed.) 1981. *Rock Characterisation, Testing and Monitoring: ISRM Suggested Methods*. Pergamon Press, Oxford.

Fitzner B. 1988. Porosity properties of naturally or artificially weathered sandstones. In Ciabach J, (ed.) *6th International Congress on Deterioration and Conservation of Stone*. Torun, Poland, N. Copernicus University, 236–245.

Franklin JA, Chandra R. 1972. The slake durability test. *International Journal Rock Mechanics Mining. Science* **9**, 325–341.

Goudie AS. 1974. Further experimental investigation of rock weathering by salt and other mechanical processes. *Zeitschrift fur Geomorphologie Supplementband*, **21**, 1–12.

Goudie AS, Allison RJ, McLaren SJ. 1992. The relations between modulus of elasticity and temperature in the context of the experimental simulation of rock weathering by fire. *Earth Surface Processes and Landforms* **17**, 605–615.

Goudie AS. 1999. Experimental salt weathering of limestones in relation to rock properties. *Earth Surface Processes and Landforms* **24**, 715–724.

Irfan TY, Dearman WR. 1978. The engineering petrography of a weathered granite in Cornwall, England. *Quarterly Journal Engineering Geology* **11**, 233–244.

Kranz RL. 1983. Microcracks in rocks: A review. *Tectonophysics*, **100**, 449–480.

La Iglesia A, Gonzalez V, Lopez-Acevedo V, Viedma C. 1997. Salt crystallisation in porous construction materials I: Estimation of crystallisation pressure. *Journal of Crystal Growth* **177**, 111–118.

Lienhart DA, Stransky TE. 1981. Evaluation of potential sources of riprap and armor stone – methods and considerations. *Bulletin of the Association of Engineering Geologists* **18** (3), 323–332.

Matsuoka N. 1990. Mechanisms of rock breakdown by frost action: an experimental approach. *Cold Regions Science and Technology* **17**(3), 253–270.

McGreevy JP. 1982. *Some Field and Laboratory Investigations of Rock Weathering with Particular Reference to Frost Shattering and Salt Weathering*, Unpublished PhD Thesis, Queens University, Belfast.

McGreevy JP. 1996. Pore properties of limestones as controls on salt weathering susceptibility: a case study. In Smith BJ, Warke PA, (eds) *Processes of Urban Stone Decay*. Donhead Publishing, Shaftesbury, 150–167.

Mortimore RN, Fielding PM. 1990. The relationship between texture, density and strength of chalk. In *Chalk*, Thomas Telford, London, 109–124.

Mottershead DN, Pye K. 1994. Tafoni on coastal slopes, south Devon, UK. *Earth Surface Processes and Landforms* **19**, 543–563.

Moye DG. 1955. Engineering geology for the snowy mountain scheme. *Journal of Institution of Engineers, Australia* **27**, 287–298.

Murphy W, Inkpen RJ. 1996. Alteration of geotechnical properties of Portland limestone and Monks Park limestone under simulated weathering. In Riederer J, (ed.) *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone (Vol. 2)*. Berlin, 739–750.

Nicholson DT, Nicholson FH. 2000. Physical deterioration of sedimentary rocks subjected to experimental freeze thaw weathering. *Earth Surface Processes and Landforms* **25**, 1295–1307.

Ordonez S, Fort R, Garcia del Cura MA. 1997. Pore size distribution and the durability of a porous limestone. *Quarterly Journal Engineering Geology* **30**, 221–230.

Pollard DD, Aydin A. 1988. Progress in understanding jointing in the past century. *Geological Society America Bulletin* **100**, 1181–1204.

Pombo-Fernandez S. 1999. *Factors Influencing Salt Induced Weathering of Building Sandstone*. Unpublished PhD Thesis, Robert Gordon University, Aberdeen.

Remy JM, Bellenger M, Homand-Etienne F. 1994. Laboratory velocities and attenuation of P-waves in limestones during freeze-thaw cycles. *Geophysics* **59** (2), 245–251.

Simmons G, Richter D. 1976. Microcracks in Rocks. In Strens RGJ, (ed.) *The Physics and Chemistry of Minerals and Rocks*. J. Wiley & Sons, Chichester, 105–137.

Tugrul A. 1997. Change in pore size distribution due to weathering of basalts and its engineering significance. In Marinos PG, Koukis GC, Tsiambaos GC, Stournara GC, (eds) *Engineering Geology and the Environment*, Volume 1. Balkema, Rotterdam, 419–424.

Underwood EE. 1970. *Quantitative Stereology*. Addison-Wesley Publishing Company, Reading.

Washburn EW. 1921. Note on a method of determining the pore-size distribution in porous material. *Proceedings of the National Academy of Sciences USA*, **7**, 115–116.

Whalley WB, Douglas GR, McGreevy JP. 1982. Crack propagation and associated weathering in igneous rocks. *Zeitschrift fur Geomorphology* **26** (1), 33–53.

Williams RBG, Robinson DA. 1998. Weathering of sandstone by alunogen and alum salts. *Quarterly Journal Engineering Geology* **31**, 369–373.

Winslow DN, Lovell CW. 1981. Measurements of pore size distribution in cements, aggregates and soils. *Powder Technology* **29**, 151–165.

FIGURE AND TABLE CAPTIONS

Table 1 Source and lithological details of rocks used in this study

Table 2 Pre-test mean*³ sample data

Table 3 Pre and post-test data from mercury intrusion porosimetry

Table 4 Deterioration indicators for each experimental weathering test

Table 5 Pre and post-test effective porosity and dry bulk density

Figure 1 Scanning electron micrographs of the five limestones

Figure 2 Schematic representation of fracture density measuring grid superimposed on a standard cylindrical specimen.

Figure 3 Pre-test pore size distributions for the limestones tested

Figure 4a–d Weight loss due to experimental weathering of five limestones

Figure 5a–c Fracture density due to experimental weathering of five limestones

Figure 6 Percentage change in effective porosity due to freeze-thaw
(*Absolute effective porosity is plotted for SpaL because of the low values involved)

Figure 7 Post-test scanning electron micrographs of the five limestones

Figure 8 Percentage change in effective porosity due to salt weathering
(*Absolute effective porosity is plotted for SpaL because of the low values involved)

Figure 9 Percentage change in effective porosity due to wetting and drying

Figure 10 Percentage change in effective porosity due to slake durability

ROCK NAME	SAMPL E CODE	LITHOLOGICAL DESCRIPTION	SAMPLE SOURCE
Low density chalk	LdCh	Heterogeneous, low density soft chalk containing fossils, deformation structures, stylolites and incipient fractures.	Upper Cretaceous Chalk of Lewes Nodular Chalk Beds, Lewes, Sussex
Magnesian limestone	MagL	Very fine, moderately weathered (classification after Moye 1955) crystalline limestone containing many small cavities and voids, stylolites and incipient fractures.	Permian dolomitic limestone from near Leeds, West Yorkshire
Oolitic limestone	OoL	Medium to coarse grained, slightly to moderately weathered oolite containing many fossils, shell fragments and large cavities, and rare incipient fractures.	Jurassic limestone from Hovingham, North Yorkshire
High density chalk	HdCh	Uniform hard to very hard chalk (Mortimore and Fielding 1990) containing large fossil fragments and stylolites. Rarely contains calcite veins and isolated voids.	Upper Cretaceous Chalk of the Flamborough formation from North Yorkshire
Sparry limestone	SpaL	Strong, dense, highly fossiliferous limestone containing many 1-2mm wide, closed calcite veins, often slightly weathered. Some stylolites and deformation structures are also present.	Carboniferous Scar Limestone from Faulds Brow, north Cumbria

Table 1 Source and lithological details of rocks used in this study

	LdCh	MagL	OoIL	HdCh	SpaL
Dry bulk density (Mg/m ³)	1.743	1.621	2.160	2.007	2.663
Effective porosity (%) of each individual cylinder used in testing	35.6	14.4	17.5	23.2	0.5
	32.8	14.6	16.0	22.3	0.0
	33.5	14.3	19.0	22.1	0.5
	34.2	14.8	17.4	22.5	0.5
	34.7	14.7	16.2	23.0	0.6
	31.7	14.2	18.1	20.3	0.5
	30.4	14.6	17.9	22.2	0.5
	31.7	14.1	15.8	23.2	0.5
	38.1	13.9	13.4	18.9	0.5
	31.5	14.6	18.8	23.4	0.6
	32.1	18.1	17.1	20.0	0.8
	37.0	14.3	14.0	22.8	0.6
	31.9	18.2	11.7	22.5	0.5
	30.2	16.8	14.1	23.8	0.5
	33.0	25.6	19.0	22.1	0.7
	34.3	16.7	18.5	22.7	0.4
	34.1	15.4	16.7	21.7	0.9
	35.5	26.6	18.7	20.2	0.4
	33.1	16.1	21.5	21.9	0.8
	33.2	15.8	19.3	22.6	0.9
34.3		20.5	22.7		
32.9			24.6		
32.5			22.3		
34.6			22.6		
33.7			25.1		
			22.9		
			24.7		
			24.7		
			23.3		
Mean effective porosity n_e (%)	33.2	14.4	17.0	22.0	0.47
Compressive strength* ¹ C_o (MPa)	6.64	7.77	11.56	46.95	79.72
Modulus of rupture* ² T_{mr} (MPa)	2.8	2.3	5.81	8.67	17.26
Point load strength* ¹ IS_{50} (MPa)	0.75	0.62	1.00	3.07	5.19
P-wave velocity* ¹ V_p (ms ⁻¹)	1966	2134	3616	3544	6239
S-wave velocity* ¹ V_s (ms ⁻¹)	1911	1104	1526	1678	2139
Young's dynamic modulus E_{dyn} (GPa)	9.44	5.23	14.04	15.33	35.03

*1 Obtained following Brown (1981); *2 obtained following Brook (1990, 1993);

*3 all values are means except n_e data for individual cylindrical specimens.

Table 2 Pre-test mean*³ sample data

PORE PROPERTY	LdCh	MagL	OoIL	HdCh	SpaL
Unweathered specimens					
Effective porosity of n_m test cube* ¹	36.1	16.2	16.8	24.7	0.52
n_m (%)	38.6	33.6	7.6	24.2	0.60
ρ_m (g/cm ³)	1.61	1.82	2.48	2.01	2.68
μn_m (%)	65.6	75.3	93.2	99.6	18.2
ϕ (μm)	1.014	0.353	0.570	0.406	-
Post freeze-thaw test					
n_m (%)	32.3	40.7	18.3	24.5	
ρ_m (g/cm ³)	1.84	1.58	2.19	2.03	
μn_m (%)	93.2	49.9	68.2	99.8	
ϕ (μm)	0.848	0.618/ 2.982	0.571/ 2.752	0.488	
Post salt weathering test					
n_m (%)	22.2	42.1	15.5	25.3	0.32
ρ_m (g/cm ³)	2.06	1.58	2.25	2.00	2.68
μn_m (%)	95.0	69.0	93.5	99.5	0.00
ϕ (μm)	0.458	0.618	0.458	0.415	-

*¹ For comparison with data for main test cylinders given in Table 2; n_m = porosity; ρ_m = dry bulk density; μn_m = microporosity based on % pores <1.0 μm ; ϕ = modal pore diameter;

Table 3 Pre and post-test data from mercury intrusion porosimetry

DETERIORATION INDICATOR	LdCh	MagL	OoIL	HdCh	SpaL
Post freeze-thaw test					
Weight loss %	54.5	7.8	84.1	28.9	0.23
Δ Fracture density mm ² /mm ³ x 10 ³	87.9	17.9	113.1	66.4	13.2
Post salt weathering test					
Weight loss %	40.3	4.7	-0.39	-4.6	0.00
Δ Fracture density mm ² /mm ³ x 10 ³	130.5* 1	75.0	23.0	115.5	15.1
Post wetting and drying test					
Weight loss %	0.12			0.00	
Δ Fracture density mm ² /mm ³ x 10 ³	1.7			0.00	
Post slake durability test					
Slake durability index %	78.9	96.0	95.4	96.0	99.7

**1 Based on 3 cycles only due to severe disintegration*

Table 4 Deterioration indicators for each experimental weathering test

Data*		LdCh	Mag L	OoIL	HdC h	SpaL
Freeze-thaw						
Pre	n _e	34.17	14.57	17.22	21.96	0.42
FT	ρ	1.737	1.628	2.153	2.010	2.664
Post	n _e	33.59	15.59	17.55	24.94	0.24
FT	ρ	1.775	1.628	2.120	2.006	2.687
Salt weathering						
Pre	n _e	32.69	14.28	16.61	22.49	0.53
MS	ρ	1.749	1.614	2.172	2.008	2.661
Post	n _e	26.71	12.94	16.04	20.23	0.11
MS	ρ	1.900	1.634	2.224	2.117	2.681
Wetting and drying						
Pre	n _e	32.85	-	-	21.72	-
WD	ρ	1.742	-	-	2.002	-
Post	n _e	32.22	-	-	25.04	-
WD	ρ	1.738	-	-	2.012	-
Slake durability						
Pre	n _e	33.83	18.36	17.40	23.55	0.65
SD	ρ	1.657	1.662	2.203	2.019	2.687
Post	n _e	34.18	17.90	17.37	21.55	0.67
SD	ρ	1.663	1.650	2.197	2.020	2.693

* FT = Freeze-thaw; MS = salt weathering (magnesium sulphate);
WD = wetting and drying; SD = slake durability

Table 5 Pre and post-test effective porosity and dry bulk density