Exploring the hot mixing and 'etching' of aggregate hypothesis

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Etching of aggregate grains during hot mixing of lime mortars is rumoured to occur and to enhance the binder–aggregate bond, but this hypothesis is currently unsupported by evidence. Experimental work was carried out to test this etching hypothesis. Hydrochloric acid diluted to 0.5 M was used to separate the quartz aggregate from four cured mortar samples: a lime putty-based mortar, a hot-mixed quicklime slaked dry and used cold, a hot-mixed quicklime slaked wet and used cold, and a hot-mixed quicklime slaked wet and used hot. Scanning electron microscopy (SEM) imaging was employed to check for signs of etching on aggregate surface morphology on both the hot-mixed and lime putty mortars. There were no visible signs of etching on the aggregate grains in any of the mortars imaged at magnifications of ×25 to ×1000. There was not sufficient evidence in these images to support the hypothesis that the hot mixing process etches quartz aggregate.

Introduction

This paper looks at the theory relating to hot mixing of lime-based mortars and its speculated ability to etch aggregate surfaces. It reviews published articles indicating that hot mixing of lime-based mortars can etch aggregate surfaces, before presenting experimental data to test this hypothesis. The experimental procedure used SEM imaging to look for evidence of aggregate etching on quartz aggregate. The results are part of ongoing research into the properties and performance of hot-mixed mortars at the University of Bath, in collaboration with Historic England.

The hot mixing and 'etching' hypothesis

Hot mixing is a mortar production technique in which quicklime is slaked in contact with aggregate. With the addition of just enough water to slake the lime, a dry hydrate can be created and stored for later use. When the mortar is needed, further water is added to the dry mix to create a workable mortar. If excess water (more than is needed simply to slake the lime) is added from the outset, then the mixing process will result in a workable mortar for immediate use. The resultant wet-slaked mortar may be used while it is still hot or, if it is non-hydraulic or feebly hydraulic, it may be left to cool before use.

There are a number of hypotheses that pertain to hot-mixed mortars and their improved durability and pore connectivity compared with lime putty-based mortars.[1] The 'etching' of aggregate surfaces is one such hypothesis. It suggests that etching occurs as a result of both the high pH and heat generated during the slaking process. This, in turn, creates a mechanical key and thus enhances the mortar's binder–aggregate bond.[2,3,4] However, there is limited published evidence to show that hot mixing improves the mortar's mechanical strength. On the contrary, studies demonstrate that hot-mixed mortars have reduced mechanical strength. For example, Válek and Matas[5] found that the pore structure induced by the slaking process reduced the compressive and tensile strength of hot-mixed non-hydraulic mortars compared with mortars made with lime putty and dry hydrate. This is supported by Lawrence et al,[6] who tested the 28-day compressive strength of non-hydraulic lime mortars. They tested mortars made using four-month-old lime putty, 20-year-old lime putty, dispersed hydrated lime putty, dry hydrated lime and kibbled quicklime for the binders. Each binder was used in three mortar mixes with three different aggregates. These aggregates were crushed bioclastic limestone, crushed oolitic limestone and silicate sand, with quartz contents of 13.76 per cent, 2.27 per cent and 97.16 per cent, respectively. The results for the hot-mixed lime mortars tested by Lawrence et al[7] were consistently lower than the four-month-old and 20-year-old lime putty mortars across all three aggregate types. When compared with the compressive strengths of the dispersed lime putty and dry hydrate mixes, the hot-mixed mortars performed better when they were made using either of the two limestone aggregates, but were weaker when made with silicate sand.

Despite hot-mixed mortars having lower mechanical strength than lime putty mortars and similar mechanical strength to non-hydraulic dry hydrate mortars, it is worth considering the etching hypothesis. This is because compressive strength is not the only measure of mortar durability or suitability for particular applications, nor is there necessarily a direct relationship between binder–aggregate bond and compressive strength in mortars prepared using different forms of lime and different mixing methods. Indeed, compressive strength is influenced by several other factors, including workmanship, workability, curing conditions, water–binder ratio, moisture suction and porosity.[8] For example, increasing the porosity in a cured mortar has been shown to lower compressive strength.

Válek and Matas[9] tested the compressive strength of non-hydraulic mortars and compared the mechanical strength with the mortar's porosity. For hot-mixed mortars, they found that increasing the binder–sand ratio increased porosity and significantly reduced compressive strength. However, the same was not true for the dry hydrate mortars, where the compressive strength increased with higher porosity. This demonstrates that porosity is only one factor that influences compressive strength. It is, therefore, possible that etching occurs and contributes to an enhanced binder–aggregate bond (and potentially improved durability) in hot-mixed mortars, but that other physical properties of those mortars lead to the reduced compressive strengths observed. Further research and understanding of the etching hypothesis will enable the industry to either take advantage of this phenomenon when making mortars, or cease circulating the currently unsupported theory.

Practical examples of etching

From the four examples in Table 1 (overleaf), we can define the etching hypothesis as: 'An early stage alteration to the surface topology of aggregates caused by high pH and/or elevated temperatures generated during slaking lime with aggregate, which leads to an improved binder–aggregate bond.'

Etching hypothesis example	Reference
'… it facilitates the caustic lime to etch onto and have a greatly improved connection to the aggregate.'	G. Lynch, 'Hot-mixed lime mortars and traditionally constructed brickwork', *The Journal of the Building Limes Forum*, 24, 2017, p. 47
'During the mixing process the action of the hot caustic lime on silica sand can potentially etch the surface of otherwise unreactive silica grains.'	The Scottish Lime Centre, *Technical Advice Note 1: Preparation and Use of Lime Mortars*, 2003, p. 28
'As the chemical reaction occurs, the alkalinity of the mix increases causing the mix to become very caustic. This enables the lime to etch into the sand, creating a very good bond between binder and aggregate.'	The Society for the Protection of Ancient Buildings, *SPAB Briefing: Lime*, 2015, p. 17
'It has also been speculated that the combination of heat and alkalinity leads to an 'etching' of the surface of aggregate grains, creating a stronger bond than would be achievable in mortars mixed with previously slaked lime, although this remains unverified.'	C. Torney, *Lime Mortars for High Exposure Levels*, 2016. Available at: www.buildingconservation.com/articles/high-exposure-mortars/high-exposure-mortars.htm

Table 1: Etching hypothesis examples from literature

In the case of hot-mixed lime-based mortars, it is speculated that the etching of aggregates is a result of the high pH of the lime and high temperatures generated by slaking. While there is minimal laboratory evidence relating to etching in hot-mixed mortars, there exist alternative studies in broader but related topics: namely, etching of limestone, aggregate and concrete mixes. These studies show that etching can occur in the following scenarios: alkali-silica reaction (ASR), prevalent in concretes; alkali-carbonate reaction (ACR), prevalent in dolomitic limes; acid etching of limestone aggregate and concrete; and sodium hydroxide and sodium carbonate etching of quartz.

ASR is a well-documented phenomenon in concretes in which mobile alkali hydroxides of sodium and potassium react with amorphous silica. This results in expansion cracks and leads to degradation of concrete structures. It is a long-term reaction that requires water for mobilisation and is accelerated at elevated temperatures.[10] To give an indication of an ASR timescale, we can look at existing standards. The standards for testing ASR in cast mortar (ASTM C 1260) and concrete (ASTM C 1293) take 16 days and one year, respectively. However, for hot-mixed mortars, it is the early-stage effects during slaking that are considered; the definition of 'early stage' depends on the volume of quicklime being slaked, but if etching occurs the reaction will manifest within a few hours (that is, while temperatures and therefore alkalinity are at their highest), not weeks. Furthermore, the chemical mechanism of ASR suggests that it is not the cause of any etching that occurs during hot mixing. Although a pure lime mortar contains a significant proportion of the strong alkali calcium hydroxide, this alone is insufficient to complete ASR.

Wang and Gillott[11] investigated the role of calcium hydroxide in ASR. It was found to aggravate ASR, but there is still reliance on the presence of sodium and potassium. In non-hydraulic limes, the concentration of sodium and potassium would not be sufficient to initiate ASR. Furthermore, ASR concerns amorphous silica, whereas, according to The Scottish Lime Centre,[12] hot mixing has the potential to etch 'otherwise unreactive silica grains'.

ACR is similar to ASR, but applies to dolomitic aggregate inclusions. It also relies on the presence of alkalis that are not abundant in non-hydraulic limes and, like ASR, takes place over a longer timescale than the hot-mixed etching hypothesis considers.[13,14,15]

Acid etching of concrete is utilised in the construction industry for creating patterned concrete finishes.[16] Hydrochloric acid, for example, is known not to etch quartz but has been shown to etch calcite.[17] In this case, the acid etching manifests as significant material loss of the calcite, with prominent unaltered quartz grains. Lamar[18] demonstrated that acid etching can be identified using an optical microscope at magnifications of ×12 and ×18. It is, therefore, likely that if alkali etching occurred in hot-mixed mortars, the results would be observable at similarly low magnifications to those at which acid etching has been observed.

Etching can also occur with alkalis. For example, Molchanov and Prikhidko[19] studied the etching effect of sodium hydroxide and sodium carbonate solutions on a variety of quartz glasses. They measured the corrosion depth using an interference microscope and found that it was typically around 1–7 µm for the majority of glasses tested. To detect etching marks in the order of 1–7 µm using an SEM, it would need to be utilised at magnifications of around ×1000. This suggests that etching caused by hot mixing may be identifiable using SEM at magnifications of between ×12 and ×1000.

The calcium hydroxide created as a result of slaking is a strong alkali. But ASR, ACR and acid etching do not explain the hot-mixed lime etching hypothesis as they all rely on the presence of chemical elements and compounds that are unlikely to be present in lime

Mix	Description	Mix design
Quicklime slaked dry and used cold (QDC)	A hot-mixed mortar, prepared in an open tub, in which just sufficient water was added to allow the quicklime to fall to a powder. Maximum temperature reached 187°C. The mixture was then allowed to cool before being made into a mortar with the addition of more water.	1:3 mix by volume kibbled non-hydraulic quicklime to Chardstock well-graded sharp sand (0–4 mm)
Quicklime slaked wet and used hot (QWH)	A hot-mixed mortar, prepared in an open tub, in which an excess of water was used to slake the quicklime and blend with the aggregate to create a mortar. Maximum temperature reached 81°C. This was then cast into moulds while hot.	1:3 mix by volume kibbled non-hydraulic quicklime to Chardstock well-graded sharp sand (0–4 mm)
Quicklime slaked wet and used cold (QWC)	A hot-mixed mortar, prepared in an open tub, in which an excess of water was used to slake the quicklime and blend with the aggregate to create a mortar. Maximum temperature reached 104°C. This was then allowed to cool before being re-worked and cast into moulds.	1:3 mix by volume kibbled non-hydraulic quicklime to Chardstock well-graded sharp sand (0–4 mm)
Lime putty (LP2)	A mortar made with mature lime putty	1:2 mix by volume one year matured non-hydraulic lime putty to Chardstock well-graded sharp sand (0–4 mm)
Water-washed fresh aggregate	Aggregate that was washed in water only, no hydrochloric acid	Quartz aggregate (0–5 mm)
Hydrochloric acid (HCl)-washed fresh aggregate	Aggregate that was washed in hydrochloric acid diluted to 0.5 M to check for etching due to hydrochloric acid	Quartz aggregate (0–5 mm)

Table 2: Descriptions of mortars and fresh aggregates analysed using SEM

mortars. An alkaline reaction of calcium hydroxide with silica is the remaining explanation to be pursued.

The following describes the tests and imaging techniques used to look for evidence of etching in hot-mixed mortars.

Materials and methods for testing

A check for hydrochloric acid etching on quartz aggregate and a test for hot-mixed etching on siliceous Chardstock sand extracted from hot-mixed mortar samples were conducted. The hot-mixed etching experimental work was carried out using cured lime mortar samples prepared in four different ways. To test for hydrochloric acid etching of quartz aggregate, fresh aggregate and fresh aggregate washed in hydrochloric acid were also examined. The six samples are described in Table 2.

To determine if etching had occurred in the hot-mixed mortar samples, the binder surrounding the aggregate particles was dissolved, and individual aggregate particles were isolated and imaged using the SEM. Initially, the four mortar samples were manually crushed to particles of around 5 mm in diameter. These samples were placed in a conical flask containing hydrochloric acid diluted to 0.5 M to dissolve the lime binder, and stirred with a manual glass stirrer for up to 20 minutes each, until they were perceived to be free from binder. To check for any etching due to hydrochloric acid, a fresh quartz aggregate from an alternative source was also stirred in hydrochloric acid diluted to 0.5 M for up to 20 minutes. A further sample of the alternative quartz aggregate was obtained but not exposed to hydrochloric acid to provide a comparison. Prior to SEM imaging, each aggregate sample was separated by filtering, washed three times with water and dried in an oven at 50°C, until a change in mass <0.2 per cent over a one-hour period was reached. SEM imaging was then carried out on particle surfaces using a JEOL SEM6480LV. Aggregate particles were coated with gold to prevent surface charging and to allow a higher resolution image to be obtained. In total, six samples were analysed.

No.	Feature	Description
1	Solution pit	Voids up to 10 μm in diameter that result from chemical activity
2	Bulbous edges	Protruding edges on rounded particles following parabolic curves
3	Crescentic ridges	Curved fractures caused by grain collision
4	Adhered particles	Smaller particles attached to the grain being analysed
5	Crater	Depressions induced by impact or circular fractures due to weakening from mineral inclusion trails
6	Crack	Induced by impact
7	Upturned plates	Induced by impact, exposing parallel plates that are oriented at an angle to the surface. These may be weathered
8	Mineral inclusion trail	Similar to solution pits but follow an alignment. Mineral inclusions create a weakening that can form fractures along this line
9	Conchoidal fracture	Shell-like curved fracture patterns
10	Solution crevasses	Similar to solution pits. Surface cracks up to 10 μm in depth that result from chemical activity
11	Linear grooves	Linear and parallel indents caused by grain collision
12	Angular features	Sharp edges
13	Scaling	Flaking off due to chemical reactions

Table 3: Descriptions of quartz surface textural features

No.	Feature	Feature frequency	
		Water-washed aggregate	HCl-washed aggregate
1	Solution pit	+++	+++
2	Bulbous edges	++	-
3	Crescentic ridges	+	-
4	Adhered particles	++	++
5	Crater	++	++
6	Crack	+	-
7	Upturned plates	++	++
8	Mineral inclusion trail	-	+++
9	Conchoidal fracture	-	+
10	Solution crevasses	-	+++
11	Linear grooves	-	++
12	Angular features	-	-
13	Scaling	-	-

+++ abundant, **++** common, **+** sparse, **-** not identified

Table 4: Surface textural features identified through SEM images of water-washed and HCl-washed aggregate. Here, 'abundant' means the feature occurs multiple times across all imaged grains, 'common' means the feature occurs multiple times but not across all imaged grains, and 'sparse' means the feature occurs on one imaged grain.

Results

A total of 56 SEM images were taken across the six aggregate samples at magnifications between ×25 and ×1000. Notable and representative images are shown in Figures 1 to 6. Figure 1 (a to d) shows the water-washed aggregate and Figure 2 (a to e) shows the HCl-washed aggregate. For each sample, a minimum of five individual aggregate grains were analysed. The grain boundary for 64 per cent of the aggregate grains is rounded. Examples of these rounded grains are shown at a lower magnification of ×25 in Figure 1 (a and b) and Figure 2 (a and b). At this magnification, the surfaces of the aggregate in Figure 1 (a) and Figure 2 (a) can be described as high relief, meaning they have topographical irregularities that measure >2 μm. The surfaces shown in Figure 1 (b) and Figure 2 (b) can be described as medium relief, meaning they have topographical irregularities that measure <1 μm. Further surface features have been identified at magnifications of ×25, ×100 and ×1000. These are described in Table 3, in line with guidance on quartz surface textural analysis by Mahaney[20] and Vos et al.[21] The feature frequency is given for both aggregate samples in Table 4. Figures 1 and 2 show these features marked by identifiers.

Of these features, the solution pits, mineral inclusion trails, solution crevasses and scaling are a result of chemical reactions. Solution pits were found in both water-washed and HCl-washed samples, but the mineral inclusion trails and solution crevasses were only identified on the samples exposed to hydrochloric acid, which is known to dissolve carbonates and iron oxides but not to etch quartz.[22] The mineral inclusion trails and solution crevasses observed may be the result of hydrochloric acid etching the aggregate surface by reacting with mineral impurities. This suggests that if carbonates and iron oxides are present as impurities in quartz aggregate, then hydrochloric acid diluted to 0.5 M may have an etching effect on the aggregate surface at low exposure durations of less than 20 minutes.

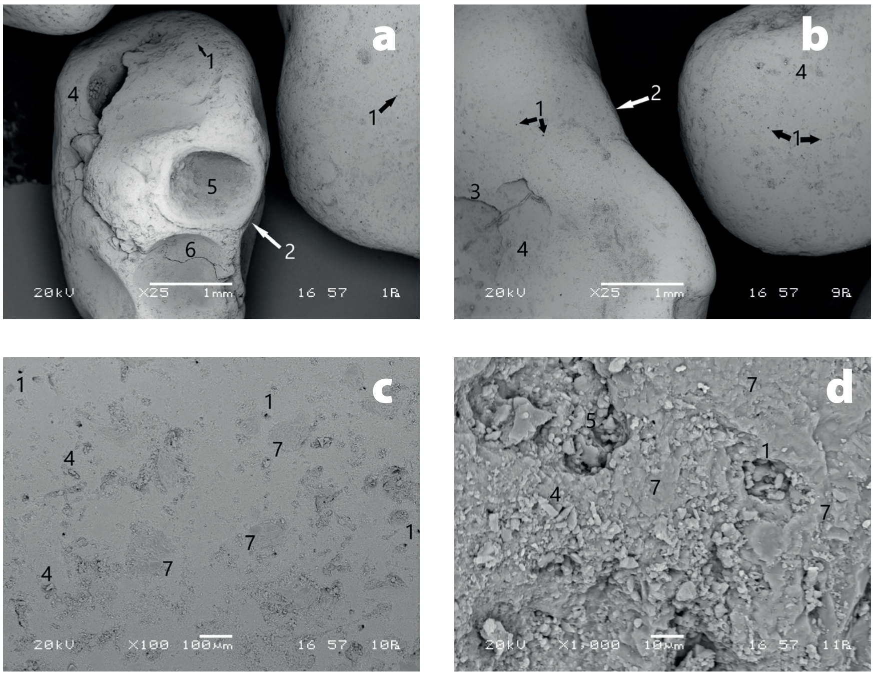

Fig. 1 SEM images of aggregate surfaces from samples of water-washed fresh aggregate: **(a)** at x25 showing solution pits [1], a bulbous edge [2], adhered particles [4], craters [5] and a crack [6]; **(b)** at x25 showing solution pits [1], a bulbous edge [2], crescentic ridges [3] and adhered particles [4]; **(c)** at x100 showing solution pits [1], adhered particles [4] and upturned plates [7]; and **(d)** at x1000 showing solution pits [1], adhered particles [4] and upturned plates [7].

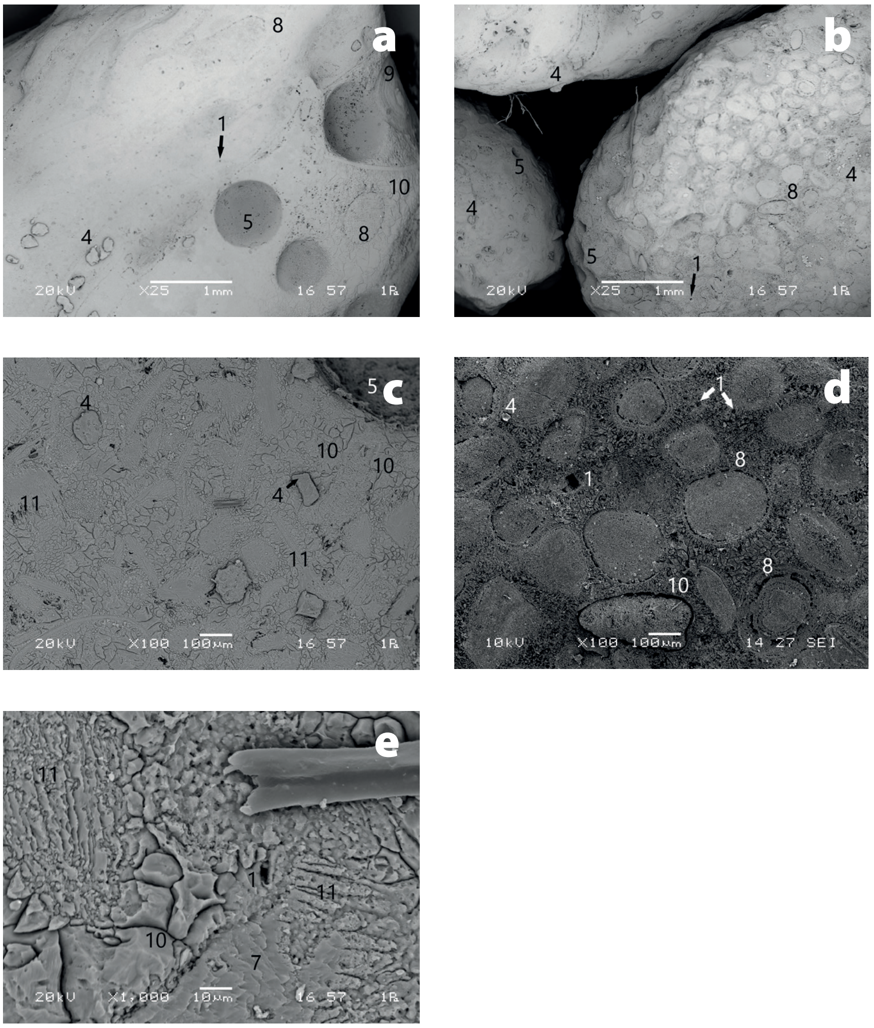

Fig. 2 SEM images of aggregate surfaces from samples of HCl-washed fresh aggregate: **(a)** at ×25 showing solution pits [1], adhered particles [4], craters [5], mineral inclusion trails [8], a conchoidal fracture [9] and solution crevasses [10]; **(b)** at ×25 showing solution pits [1], adhered particles [4], craters [5] and a mineral inclusion trail [8]; **(c)** at ×100 showing adhered particles [4], a crater [5], solution crevasses [10] and linear grooves [11]; **(d)** at ×100 showing solution pits [1], an adhered particle [4], mineral inclusion trails [8] and a solution crevasse [10]; and **(e)** at ×1000 showing a solution pit [1], upturned plates [7], solution crevasses [10] and linear grooves [11].

No.	Feature	Feature frequency			
		LP2	QDC	QWC	QWH
1	Etching – solution pit	+++	++	+++	++
2	Bulbous edges	-	-	-	-
3	Crescentic ridges	+	++	-	-
4	Adhered particles	+++	+	++	++
5	Crater	++	+++	+++	+++
6	Crack	-	+++	-	+
7	Upturned plates	+	+	++	+
8	Etching – mineral inclusion trail	+	+	-	-
9	Conchoidal fracture	-	-	+	-
10	Etching – solution crevasses	-	-	-	-
11	Linear grooves	+	-	-	-
12	Angular features	++	++	+	++
13	Etching – scaling	+	-	+	-

+++ abundant, **++** common, **+** sparse, **-** not identified

Table 5: Surface textural features identified through SEM images of LP2, QDC, QWC and QWH aggregate. Here, 'abundant' means the feature occurs multiple times across all imaged grains, 'common' means the feature occurs multiple times but not across all imaged grains, and 'sparse' means the feature occurs on one imaged grain.

Figures 3 to 6 show representative SEM images from samples LP2, QDC, QWC and QWH. For each sample, a minimum of eight individual aggregate grains were analysed. The grain boundary for 82 per cent of the aggregate grains was angular. Examples of these angular grains from samples LP2, QDC, QWC and QWH are shown in Figures 3 to 6 at low magnifications of ×25 and ×27. At this magnification, the surface of these samples can predominately be described as high relief. Surface features have been identified at magnifications of ×25 and ×1000. They are described in Table 3, and the feature frequency is given for all four aggregate samples in Table 5. The images in Figures 3 to 6 show these features marked by identifiers.

Images in Figure 3 (a to f) are of LP2 aggregate. The particle in Figure 3 (a) has some remaining lime binder after the rest of the binder was dissolved in hydrochloric acid. Image analysis shows that lime putty-based mortar (LP2) had an abundance of adhered particles, which was greater than the frequency of adhered particles in the three hot-mixed mortars (QDC, QWC and QWH). There is some surface contamination in Figure 3 (d), which is from the filter paper used during sample washing. Similar surface contamination is present in Figure 6 (b) and Figure 2 (e). These are not included in Table 4 or Table 5 because they are not considered to be mechanical or chemical features of the aggregate surface. Another abundant feature seen in Figure 3 (a to f) is the presence of solution pits, which are a result of chemical processes. A mineral inclusion trail was identified in Figure 3 (d) and some scaling can be seen in Figure 3 (e). These two infrequent features are indicators of chemical processes.

The frequency of the chemically induced features can be compared in the lime putty-based mortar and the three hot-mixed mortars to assess the effect of hot mixing on quartz aggregate surfaces. It is worth noting that these features may exist due to natural processes on the grains before they were used in the mortars or due to hydrochloric acid reacting with carbonates or iron oxides. Therefore, if hot mixing etched the aggregate, we would expect to see a higher frequency of solution pits, mineral inclusion trails, solution crevasses and scaling in the hot-mixed samples than in the lime putty-based sample. Solution pits are prevalent in LP2 and QWC, but not as frequent in QDC and QWH. Mineral inclusion trails occur in the LP2 and QDC images only; they are not present in the QWC and QWH images. Solution crevasses are not seen in the lime putty-based mortar nor in any of the hot-mixed mortars. Scaling has only been identified in LP2 and QWC and has not been noted in QDC or QWH.

These results imply that etching features are less common in the hot-mixed mortar samples, and therefore suggest that hot mixing did not create any additional etching features on the quartz aggregate surfaces.

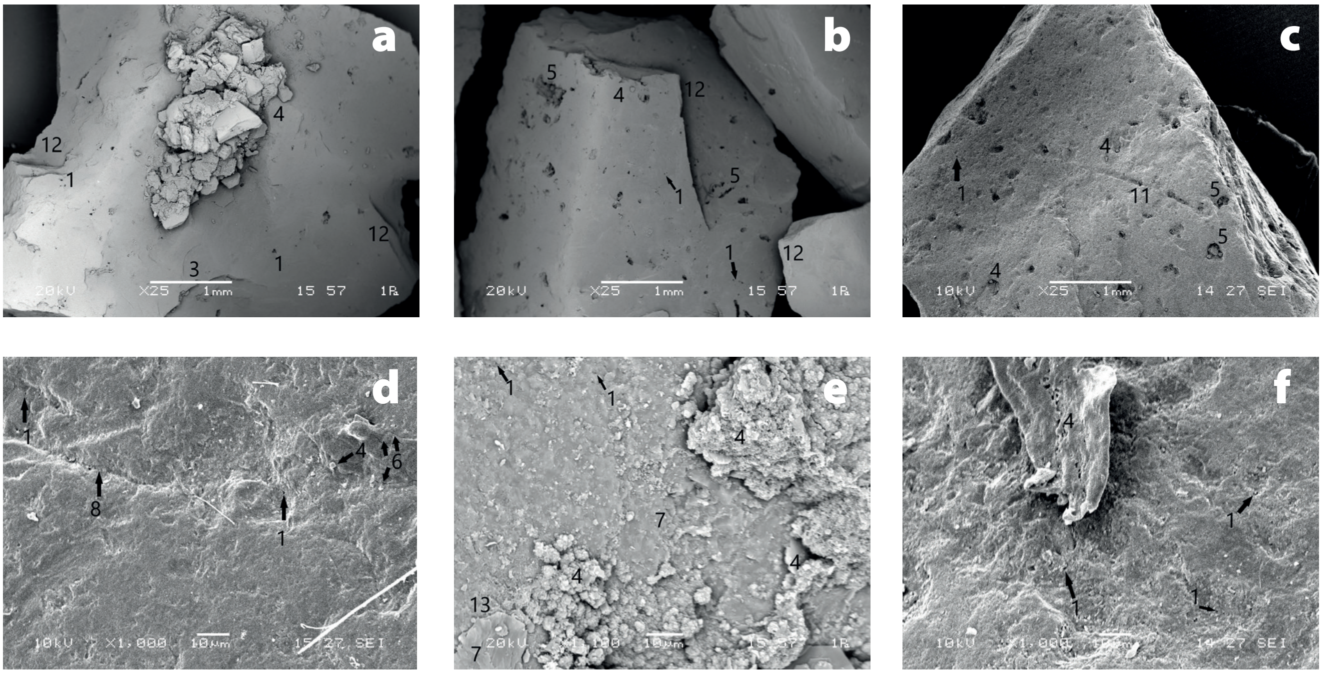

Fig. 3 SEM images of aggregate surfaces from samples of LP2 mortar: **(a)** at ×25 showing solution pits [1], a crescentic ridge [3], adhered particles [4] and angular features [12]; **(b)** at ×25 showing solution pits [1], adhered particles [4], craters [5] and angular features [12]; **(c)** at ×25 showing solution pits [1], adhered particles [4], craters [5] and a linear groove [11]; **(d)** at ×1000 showing solution pits [1], adhered particles [4], cracks [6] and a mineral inclusion trail [8]; **(e)** at x1000 showing solution pits [1], adhered particles [4], upturned plates [7] and scaling [13]; and **(f)** at ×1000 showing solution pits [1] and an adhered particle [4].

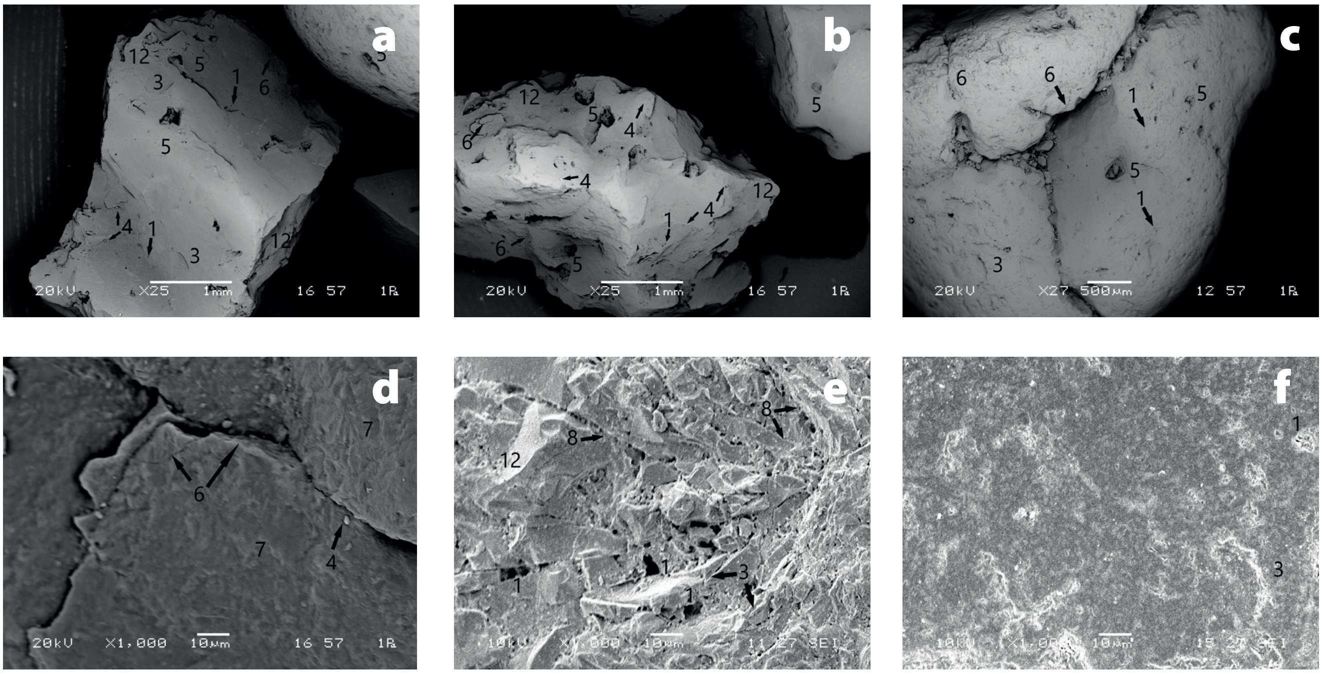

Fig. 4 SEM images of aggregate surfaces from samples of QDC mortar: **(a)** at ×25 showing solution pits [1], crescentic ridges [3], adhered particles [4], craters [5], a crack [6] and angular features [12]; **(b)** at ×25 showing solution pits [1], adhered particles [4], craters [5], a crack [6] and angular features [12]; **(c)** at ×27 showing solution pits [1], a crescentic ridge [3], craters [5] and cracks [6]; **(d)** at ×1000 showing adhered particles [4], cracks [6] and upturned plates [7]; **(e)** at ×1000 showing solution pits [1], crescentic ridges [3], mineral inclusion trails [8] and angular features [12]; and **(f)** at ×1000 showing a solution pit [1] and a crescentic ridge [3].

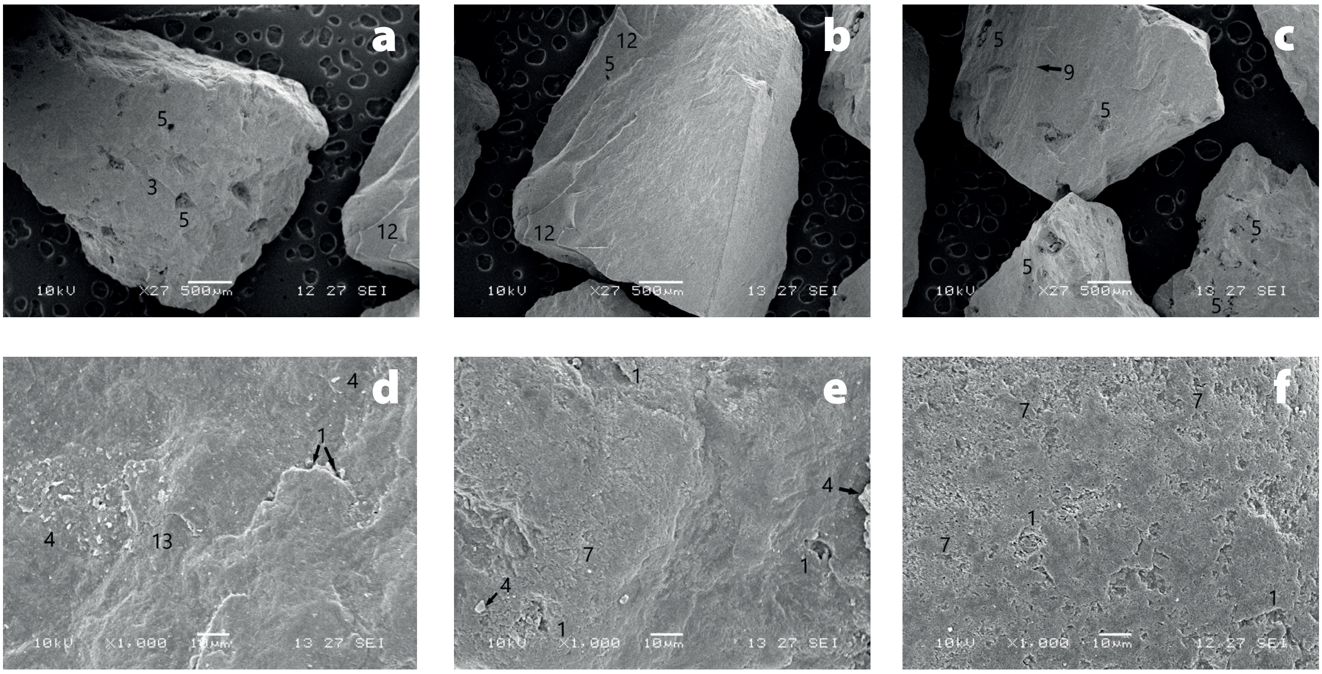

Fig. 5 SEM images of aggregate surfaces from samples of QWC mortar: **(a)** at ×27 showing a crescentic ridge [3], craters [5] and an angular feature [12]; **(b)** at ×27 showing a crater [5] and angular features [12]; **(c)** at ×27 showing craters [5] and a conchoidal fracture [9]; **(d)** at ×1000 showing solution pits [1], adhered particles [4] and scaling [13]; **(e)** at ×1000 showing solution pits [1], adhered particles [4] and upturned plates [7]; and **(f)** at ×1000 showing solution pits [1] and upturned plates [7].

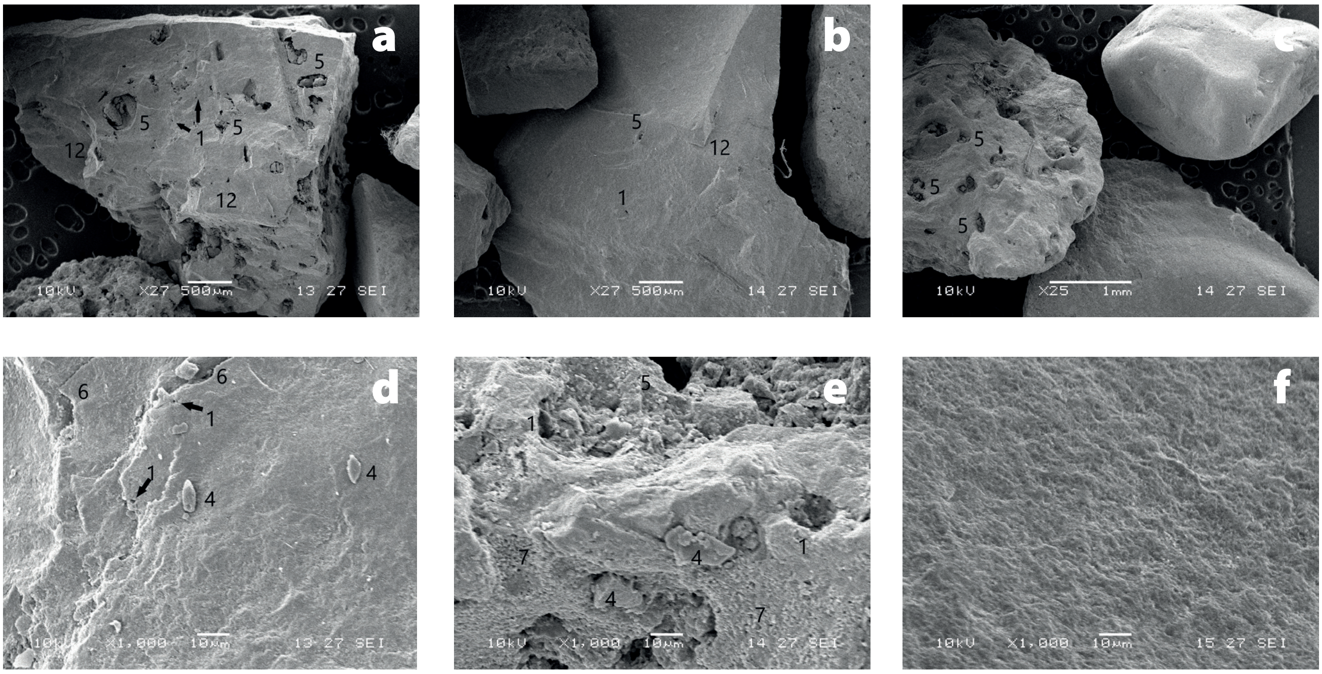

Fig. 6 SEM images of aggregate surfaces from samples of QWH mortar: **(a)** at ×27 showing solution pits [1], craters [5] and angular features [12]; **(b)** at ×27 showing a solution pit [1], a crater [5] and an angular feature [12]; **(c)** at ×25 showing craters [5]; **(d)** at ×1000 showing solution pits [1], adhered particles [4] and cracks [6]; **(e)** at ×1000 showing solution pits [1], adhered particles [4], a crater [5] and upturned plates [7]; and **(f)** at ×1000, which shows no identifiable features.

Discussion

Hydrochloric acid does not etch quartz.[23] In the HCl-washed fresh aggregate sample, there were mineral inclusion trails and solution crevasses that were not present in the water-washed fresh aggregate sample, thus suggesting that hydrochloric acid may have an effect on surface condition when observed at magnifications between ×25 and ×1000. This can be attributed to the presence of impurities such as carbonates and iron oxides. It is also possible that imaged etching features are a result of mechanical and chemical processes that occur in the aggregate's natural environment. Therefore, to check for hot-mixed etching, it was necessary to compare the surfaces of the aggregate from the lime putty mortar with those from the hot-mixed mortars. If hot mixing etches the aggregate, the images from the hot-mixed mortars would show a higher frequency of etching features.

Four types of etching features were identified across the six aggregate samples. These were solution pits, mineral inclusion trails, solution crevasses and scaling. The frequency of these four etching features across the aggregates from the lime putty mortar and the three hot-mixed mortar samples is shown in Table 5. Solution crevasses only occurred in the HCl-washed fresh aggregate. Solution crevasses were not present in aggregate samples from any of the four mortars. Of the remaining three etching features, their rates of occurrence in the aggregates from the three hot-mixed mortars were the same as or lower than in the aggregates from the lime putty-based mortar. This implies that hot mixing did not create any additional etching features on quartz aggregate surfaces. From the SEM images taken, there is insufficient evidence to support the etching hypothesis between magnifications of ×25 and ×1000. The results from these images do not support the etching hypothesis as generally described in the literature.[24,25,26,27]

This study looked at the etching effect of hot-mixed mortars on quartz aggregate. Further investigations will examine the effect on different types of aggregates. Furthermore, the hypothesis suggests that aggregate etching in hot-mixed mortars is caused by the combination of high alkalinity and high temperature, rather than by high alkalinity alone. In these samples, the hot-mixed mortars were slaked in an open tub. In such conditions, the temperature loss would be accelerated and the control of temperature would not be as precise as that of a closed system. Further investigations into the heat effects of hot mixing on etching demand a controlled closed-box test.

Conclusion

The SEM images of aggregate samples from one lime putty mortar and three hot-mixed mortars did not support the hypothesis that the slaking process etches quartz aggregate.

Acknowledgements

This study was funded by Historic England and supported by the EPSRC Centre for Doctoral Training in Decarbonisation of the Built Environment (dCarb). The authors would like to extend their thanks to Historic England for providing hot-mixed mortar samples, Colin Burns and Bill Revie for preparing the samples, and Lucie Fusade and Heather Viles for helpful discussions.

Endnotes

1 A. Forster, 'Hot-lime mortars: A current perspective', *Journal of Architectural Conservation*, 10(3), 2004, pp. 7–27. Available at: www.tandfonline.com/doi/abs/10.1080/13556207.2004.10784923

2 Ibid.

3 The Society for the Protection of Ancient Buildings, *SPAB Briefing: Lime*, 2015.

4 G. Lynch, 'Hot-mixed lime mortars and traditionally constructed brickwork', *The Journal of the Building Limes Forum*, 24, 2017, pp. 38–49.

5 J. Válek and T. Matas, 'Experimental study of hot mixed mortars in comparison with lime putty and hydrate mortars', in J. Válek et al (eds), *Historic Mortars: Characterisation, Assessment and Repair*, 2012, pp. 269–81.

6 M. Lawrence et al, 'Non-hydraulic lime mortars', *Journal of Architectural Conservation*, 12(1), 2006, pp. 7–33.

7 Ibid.

8 J. Válek and P. J. M. Bartos, 'Influences affecting compressive strength of modern non-hydraulic lime mortars used in masonry conservation', *WIT Transactions on the Built Environment*, 55, 2001.

9 Válek and Matas, 2012, op cit.

10 N. Jackson (ed), *Civil Engineering Materials*, 3rd ed, 1983.

11 H. Wang and J. E. Gillott, 'Mechanism of alkali-silica reaction and the significance of calcium hydroxide', *Cement and Concrete Research*, 21(4), 1991, pp. 647–54.

12 The Scottish Lime Centre, *Technical Advice Note 1: Preparation and Use of Lime Mortars*, 2003.

13 S. Chatterji et al, 'Studies of alkali-silica reaction.

Part 3. Mechanisms by which NaCl and $Ca(OH)_2$ affect the reaction', *Cement and Concrete Research*, 16, 1986, pp. 246–54.
14 Wang and Gillott, 1991, op cit.
15 F. H. Shrimer, *Progress in the Evaluation of Alkali-Aggregate Reaction in Concrete Construction in the Pacific Northwest, United States and Canada*, 2005.
16 E. Arntson, *Etching Primer for Concrete Floor Surfaces Containing Sulfuric Acid*, US19730322520 0110 [Patent], 1973.
17 J. E. Lamar, *Acid Etching in the Study of Limestones and Dolomites*, 1950.
18 Ibid.
19 V. S. Molchanov and N. E. Prikhidko, 'Corrosion of silicate glasses by alkaline solutions: Communication 1. Breakdown of quartz, quartz glass, and some laboratory glasses by sodium hydroxide and sodium carbonate solutions', *Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science*, 6, 1957, pp. 1179–1184.
20 W. C. Mahaney, *Atlas of Sand Grain Surface Textures and Applications*, 2002.
21 K. Vos et al, 'Surface textural analysis of quartz grains by scanning electron microscopy (SEM): From sample preparation to environmental interpretation', *Earth-Science Reviews*, 128, 2014, pp. 93–104. Available at: dx.doi.org/10.1016/j.earscirev.2013.10.013
22 Ibid.
23 J. S. Watts and G. W. Neudeck, 'Buried-gate oxide thinning during epitaxial lateral overgrowth for dual-gated metal–oxide–semiconductor field-effect transistors', *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, 14(3), 1996, p. 1670.
24 The Scottish Lime Centre, 2003, op cit.
25 The Society for the Protection of Ancient Buildings, 2015, op cit.
26 C. Torney, *Lime Mortars for High Exposure Levels*, 2016. Available at: www.buildingconservation.com/articles/high-exposure-mortars/high-exposure-mortars.htm
27 Lynch, 2017, op cit.