

HYDRATED LIME ADDITIONS TO CEMENT MORTARS; QUANTIFYING THE BENEFITS TO MORTAR DURABILITY IN MASONRY STRUCTURES

A.S. Smith¹, F. Verhelst², C. Denayer³ and R. Givens⁴

¹Head of Sustainability & Construction Materials, Ceram Research Ltd, Stoke on Trent, Staffordshire, ST4 7LQ, United Kingdom, andrew.smith@ceram.com

²Senior Marketing Manager Materials, Lhoist, rue de l' industrie, 31, B-1400 Nivelles Belgium, frederik.verhelst@lhoist.com

³Marketing Manager Construction, Carmeuse Europe, Bd de Lauzelle 65, B-1348 Louvain-la-Neuve, Belgium, christophe.denayer@carmeuse.com

⁴Technical Sales Manager, Buxton Lime & Cement, Tarmac Limited, Tunstead House, Buxton, SK17 8TG United Kingdom, richard.givens@buxtonlime.co.uk

ABSTRACT

The European Lime Association (EuLA) have instigated a project investigating the benefits associated with the addition of hydrated lime to cement based mortars, and more importantly, what gaps exist in the evidence in respect of the benefits of hydrated lime additions to workability, bond strength development, durability and in addition the modes of failure of mortars and the impact of lime additions. The project brings together experts from across Europe from both industrial, academic and commercial research & technical establishments, with the aim to produce the definitive guide on the benefits of lime addition to cement based mortars.

This paper focuses on the investigation and assesses the benefits of hydrated lime additions to cement based mortars in respect of mortar and masonry durability, namely:

- Thermal & Moisture Movement in Masonry
- Resistance to Rain Penetration
- Resistance to Salt Crystallization and Chemical Attack
- Frost Resistance

The paper reviews the existing scientific literature and reports on the need for more research to specifically investigate areas where there are tangible and measurable benefits to the performance of the cement based mortar by the addition of hydrated lime.

In addition the paper examines the underlying modifications and changes in the mortar structure and composition, and what impact this has had in the development of the physical properties being investigated.

KEYWORDS: hydrated lime, mortar, durability, rain penetration, movement, salt crystallization

INTRODUCTION

The addition of lime (hydrated lime/building lime, Ca(OH)₂) into cement based mortars has been commonplace for over 50 years, and in parts of Europe for over 100 years. The main purpose has been to provide better "workability" of the mortar in the fresh state, thus providing an easier material for the brick layer or stone layer to work with. Much of this "workability" is attributed to two modifications to the mortar when lime is added; water retention and air entrainment.

Although the water retention properties of lime additions have the potential to modify the hardened mortar properties, namely the connectivity of the pore structure, they predominately impact upon the fresh state properties, where as air entrainment modifications are in general carried over into the hardened mortar, and have been shown to have an impact upon durability, specifically with frost resistance.

Many authors infer benefits of cement mortars with lime additions for specific mortar or masonry properties such durability, however few have specifically undertaken research into the role lime itself plays. Much of the works published focus on the different performance when compared to OPC (Ordinary Portland Cement), Masonry Cement and Blended Cements, with and without air entrainment. The papers therefore generally fail to identify the causation of the benefit, namely, what role the lime has played in this modification of performance, or if the actual properties (particle size distribution, chemical composition, etc) of the lime influence the end results.

This paper focuses on the "durability" aspects of lime additions into cement based mortars, based on the published technical and scientific literature.

DURABILITY

The Building Research Establishment's (BRE) "Building Mortar" digest 362 [1] recommends the use of a "High Durability Mortar" in situations where the masonry is exposed to severe weather conditions. These siturations include where the masonry is below or near external ground levels, in freestanding boundary walls, in earth retaining walls, and in papapets and chimneys. They go on to recommend that under these conditions, an air-entrained 1:1½:4½ cement:lime:sand (C:L:S) mortar should be used.

Clearly in the late 1980's and early 1990's the BRE regarded the addition of lime to a cement:sand mortar as being important to achieve enhanced durability characteristics. This position was based principally on work undertaken by Harrison & Gaze [2] where 84 different mortar mixes were subjected to simulated freeze-thaw and wetting/drying cycles to simulate severe exposure in the UK.

They conclude that much of the actual in service durability characteristics are dictated by the composition of the mortar and the initial reaction of the placement of mortar onto the masonry unit. Key to the durability aspects of the mortar (frost resistance and resistance to sulfate attack) are the closed and connected pore structure developed as a result of air entrainment (closed and regular sized) and the irregular shaped and sized pore structure resulting from excess water in the mix. They also found that the initial rate of suction from the masonry unit has an important role to play in the eventual pore structure of the mortar.

Within the context of this report, 4 aspects of durability relating to hardened mortar and the inherent performance of masonry built with lime-cement mortars are reviewed:

- Thermal & Moisture Movement in Masonry
- Resistance to Rain Penetration
- Resistance to Salt Crystallization and Chemical Attack
- Frost Resistance

Sébaïbi et al [3] looked at the modification to the micrstructure of mortar by different types of lime and different amounts of cement substitution. They conclude that, for the majority of limes, the substitution of a small percentage of cement by lime does not modify the mocrostructure of the mortar matrix, however for a higher lime substitution percentage, the addition of lime does have an impact on the microstructure of the mortar, principally through the presence of micro cracks in the matrix or by an alternative hydrate development, a calcium hydroxide with a significant specific surface areas.

Again, the research does not develop any conclusions as to how this change in microstructure may influence the proeprties of hardened mortar.

THERMAL & MOISTURE MOVEMENT IN MASONRY

It is widely acknowledged that, in service, movement of masonry can occur as a result of either reversible thermal or irreversible moisture expansion. Irreversible moisture expansion is of particular relevance to clay masonry of specific types, where the glassy ceramic matrix is known to react with moisture resulting in an expansion of the masonry units. As this is a volumetric expansion, the impact can be seen both vertically and horizontally in the masonry itself.

Accommodation of movement is therefore of importance when considering the potential impact such movement may have upon the mortar as well as that of the masonry units.

Arandigoyen [4] identifies that the Young's Modulus for compressive strength of C:L:S mortars with varying compositions show similar characteristics, except that is for the very high lime content mortars. They report that lime rich mortars the presence of a noticeable plastic deformation zone before the mortar breaks, something not seen in the cement only mortars.

These results indicate that the presence of a high lime content in the binder contributes to the ability of the mortar to accommodate plastic deformation as well as elastic deformation before failure. Conversely the higher the cement content the more prone the mortar is to elastic deformation being followed by failure. Unfortunately, although compressive and flexural strength attributed were assessed, shear and tensile strength attributes of the mortar were not.

Zeng et al [5] work on the thermal expansion characteristics of cement pastes and mortars conclude that by increasing the porosity, the thermal expansion coefficient (TEC) is reduced, meaning that the more air voids in a mortar the less it expands as a result of thermal inputs. As lime additions are known to increase the porosity of mortars by the introduction of air voids,

therefore lime mortars are likely to expand less than mortars without the same amount of voids (pores).

Sickles Taves [6] shows that mortars containing lime, namely a 1:1:6, a 1:2:9 and a 1:3:12 C:L:S mortars all show better accommodation of movement, and conclude that lime has a direct and favourable effect, by permitting limited deformation without cracking.

The ability of cement mortars containing lime to accommodate movement, initially through elastic deformation, and then through creep, clearly has benefits, not least when considering the reaction to expansive masonry units, either thermally induced or as a result of moisture expansion.

Elastic strain and recovery plays an important role in thermal expansion and contraction of masonry, thus lime-cement mortars can be used in order to accommodate temporary applied stress. This allied with the autogenous healing capacity of these mortars, thus repairing any micro cracks generated at the time of movement, results in the maintenance of the resistance to rain penetration characteristics.

RESISTANCE TO RAIN PENETRATION

The Mortar Industry Association (MIA) promotes the use of lime additions in cement mortars for resistance to rain penetration. The MIA's Datasheet #18 [7], state that the inclusion of lime in a mortar promotes a more intimate contact between the mortar and the masonry unit. An increase in the plasticity and cohesion of the mortar also results in more effective filling of the vertical joints which subsequently resists penetration by wind driven rain better than in some non-lime mortars.

The MIA go on to state that lime also has a benefit in respect of autogenous healing properties of the mortar. They identify that when lime based mortars crack they do so in the form of micro cracks. Ingress of rainwater into these cracks results in the dissolution and subsequent deposition of calcium hydroxide, when the water evaporates. Subsequent reaction with the carbon dioxide in the air results in this lime converting to calcium carbonate, thus repairing the micro crack, as process known as autogenous healing

Mosquera et al [8] investigated the modification to the pore structure and connectivity of the pores in lime mortars with cement additions. Their work used Mercury Intrusion Porosimetry (MIP) measurements and found that in lime-based mortars, as cement content increased, the pore sizes and volumes decreased.

By inference this conclusion indicates by adding lime to cement based mortars the pores increase in size and become better connected. Connectivity of the pore structure therefore allows the movement of both vapour and liquid water, however as already identified, both cement hydration products and lime additions result in an excess of free Ca(OH)₂, which can be subsequently transported and deposited as a result of carbonation in this pore structure.

The research of Wright et al [9], carried out on the impact of lime addition on bond strength in both cement and masonry cement mortars, concluded that there was no "enhancement" of the bond with increased lime additions, however there was a reduction in compressive strength.

Work on the assessment of the resilience of masonry to wind driven rain penetration has identified that rather than the masonry units or the mortar being the dominant factor, it is the interface between the two that has the greatest influence on performance.

Goodwin & West [10] reviewed the scientific literature of its time and identified that the addition of lime to a cement mortar had a major influence on the reduction in rain penetration, as a result of the deposition of initially calcium hydroxide, which in turn carbonated to calcium carbonate, at the interface. This was attributed to the initial capillary suction of moisture from the mortar into the brick at the time of laying. Although the physical bond of the hydrated cement phase result in the strength, the deposition of these "free lime" products improves the overall performance of the mortar joint "in service".

Work presented by the National Lime Association [11] in the USA, quantified the benefits in respect of "special lime" (Type S to ASTM C207) additions to cement mortars in terms of rain penetration performance. When compared with masonry cements and blended cements to the ASTM methodology, the following results were recorded:

"Time To First Dampness Walls constructed with cement-lime mortars took 35%

to 250% longer to show signs of dampness.

First Visible Water It took approximately 350% to 575% longer for cement-

lime mortars to show signs of visible water.

Percent Dampness Cement-lime walls showed 5% to 40% less area of

dampness than seen with masonry cement mortars.

Leakage Per Panel The total amount of water leakage collected per wall

panel during the test for masonry cement assemblages was 3.5 to 15.3 times the amount collected for cement-

lime mortars."

Work by Bowler et al [12], Bowler & Sharp [13] on rain penetration through brick masonry shows that when a number of mortar combinations and high and low suction rate bricks were tested, it was clear that lime-cement mortars (1:1:5½ and 1:1:6) all performed reasonably well and better on the whole than cement sand mortars.

It was also clear that the initial rate of suction of the masonry unit, when the same mortar was tested, made a significant different. They found that high suction brick masonry has, on the whole, a lower resistance to rain penetration.

The inference made here is that high suction from the masonry units can have a detrimental impact upon the resistance to rain penetration. This could be as a result of greater porosity in the mortar itself as a result of the capillary draw of moisture out of the mortar initially, and the resulting pore structure, or as a result of removing water from the mortar and thus reducing or limiting the "hydration" process of the mortar.

In addition to the movement of moisture through a masonry structure, there is evidence that the formation of a "lime" rich layer at the interface between mortar and masonry unit can significantly reduce the capillary rise of moisture from the ground. Colantuono et al [14] show that in cement based mortars the addition of lime promotes deposition of Ca(OH)₂ (portlandite) at the interface between the mortar and the masonry units (in this case natural stone). This layer significantly reduces the capillary rise of moisture, more so than cement (OPC) mortars and blended cement based mortars, where the migration of Ca(OH)₂ from mortar towards the masonry units is less.

West et al [15] report the change in permeability of mortars with increasing lime additions, 1:1/4:3, 1:1:6 and a 1:3:12 C:L:S, shows both an increase in the 24hr cold water absorption value (with increasing lime content) and an increase in capillary uptake of water. They also shows that for any given mortar composition, the initial rate of suction of the masonry unit, in this case bricks, also has a significant influence on the mortar permeability when hardened.

RESISTANCE TO SALT CRYSTALLIZATION AND CHEMICAL ATTACK

There are 2 potential mechanisms that fall within this section of the report. Salt crystallization can be regarded as a physical process, resulting from the deposition (growth) of salts within the pore structure of the mortar, in a similar way to the formation of ice crystals during frost attack.

Chemical attack is a different process and results from the aggressive alteration of the structure or composition of the mortar. Sulfate attack is probably the most common form of chemical attack and results from the aggressive breakdown of the C3A (tri-calcium aluminate) content in the cement by soluble sulfates, resulting in the formation of an expansive calcium alumina sulfate hydrate (ettringite).

In relation to salt crystallization, Lubelli et al [16] using a 4:1:20 (1:1/4:5) mortar exposed to different NaCl levels, noted that in lime-cement mortars the presence of NaCl produces dilation during the drying phase of the relative humidity (RH) cycle, resulting in the crystallisation of the salts. Such dilation is reported as being irreversible and increases with repeated RH cycling. The resulting damage of the mortar is in the form of "sanding" or "fretting" of the outer layers, where most of the salts accumulate.

As previously mentioned, the growth of salt crystals within the pore structure of the mortar ultimately results in "fretting" only when the expansive forces imparted by the salt crystal growth, exceeds the restraining (tensile) forces of the mortar matrix itself.

The second form of soluble salt related durability issue with mortars is that of chemical attack. Although many of the chemical attack mechanisms result in the formation of an expansive reaction substance, eg ettringite in sulfate attack, the initiation of the process results from a chemical reaction between the soluble component and the mortars binder phases.

The formation of gypsum $(CaSO_4.2H_2O)$ within the surface layers of historic masonry units and mortars, has been reported for many years. This is often referred to as "fretting" and can also be found within the surface layers of the mortar.

Lubelli et al [17] reports on a link between the crystallization of the salt crystallization processes and a chemical attack process resulting in the formation of a new expansive phase in the pore structure. They identify that the reaction between CaCO₃ (calcite) and H₂SO₄ results in the formation of CaSO₄ (gypsum) and H₂CO₃. As this reaction typically takes place on the surface of the calcite grains, resulting in the formation of a gypsum layer on the surface of the calcite grains, thus limiting further reaction. However, in the presence of NaCl, the reaction changes and hydrochloric acid is formed, limiting the formation of gypsum on the calcite grain surfaces and thus promoting an ongoing reaction with the calcite grains.

In addition to ettringite formation as a result of sulfate attack, thaumasite has also been identified and the potential cause investigated by Gaze & Crammond [18]. Their work showed that a mortar containing calcium carbonate (CaCO₃) either as fine aggregate or as a product of carbonation of Ca(OH)₂ can react with magnesium or potassium sulfate solutions, resulting in the formation of thaumasite and brucite, as a result of the breakdown of the calcium-silicate-hydrate as the pH drops below pH10, in predominantly cold wet conditions <5°C.

FROST RESISTANCE

As with much of the attributes linked with lime additions to cement based mortars, there is very limited number of studies that have investigated the modification of the mortar's property, and how this benefits frost resistance. Much of the inferred benefits come from some basic attributes, already discussed in this paper, namely:

- Pore size
- Pore connectivity
- Reduced rain/water penetration
- Autogenous healing

The frost resistance of masonry tends to focus on the masonry units performance rather than the performance of the mortar, hence the development for performance characteristics and requirements for the likes of clay bricks in EN 771-1 [19], although a harmonized frost resistance test (TS 772-22 [20]) is still to be finalised. No such performance test has been developed for mortar, and within EN 998-2 [21], clause 5.4.7 still states:

"Until a European Standard method of test is available, the freeze/thaw resistance shall be evaluated and declared to the provisions valid in the intended place of use of the mortar."

Givens [22] concluded that lime additions to cement mortars (1:1:6) provided both enhanced resistance to frost damage but also to the combined frost and sulfate attack, especially when the C3A (tri calcium aluminate) content of the OPC is <9%.

Bowler [23] looked at both early "green stage" fresh mortars and hardened mortars in respect of the role air entrainment has upon this aspect of durability. He comments that the action of early suction, like the coarse pores imparted by air entraining agents, protects the hardened mortar from damaging frost action.

Whilst there appears to be a significant amount of anecdotal evidence that lime additions to mortars are beneficial to frost resistance, there is little direct scientific evidence, not least as there is no standard test method developed to assess frost resistance.

DISCUSSION

Although durability is one of the key benefits observed by the addition of lime to cement based mortars, the actual evidence from research and scientific papers into the benefits and causation are very limited, as highlighted in this paper.

The majority of the anecdotal evidence relates to the modification of "green or fresh state" mortars, namely, modifications to the pore structure and its connectivity, along with the reduction in "brittleness" of the mortar bonds and subsequent infilling of micro cracks with carbonated lime (autogenous healing).

The most direct evidence of the benefits of lime relate to the rain penetration work undertaken. In this body of work, the initial placement of the fresh mortar, the initial rate of suction and transfer of Ca(OH)₂ rich pore waters into the interface zone between mortar and masonry unit, clearly reduces the potential pathways for capillary movement of moisture along this interface.

There is logical correlation between the ability of lime-cement mortars to accommodate thermal and irreversible moisture movement, resulting from the ability of the lime rich mortars to deform plastically and through creep. Coupled with the ability of autogenous healing of any micro cracks formed, this accommodation of movement also maintains the resistance to rain penetration.

The ability of lime-cement mortars to resist salt crystallization and chemical attack, whilst reported, is not clearly understood beyond the inferred evidence and logic based on the porosity, permeability and compositional change of the hardened mortar in service.

As with frost resistance, the potential damage resulting from the growth of salt crystals within the matrix of the mortar, is related directly to 3 factors:

- Water soluble salts being present and mobile within the masonry.
- Deposition of the salts within the pore structure of the mortar.
- Tensile strength of the mortar.

Therefore the absorption and deposition (crystallization) of the salts is significantly impacted upon by the pore size and connectivity. Lime appears to protect the mortar by increasing the mean void size, however higher lime contents also reduce the tensile strength of the mortar, so there is a fine balance between these two properties.

In terms of resistance to chemical attack, the addition of lime appears fundamentally to act by dilution of the reactive components in the cement phases, specifically with sulfate attack and the formation of ettringite. Excess free Ca(OH)₂ in the pore solutions also inhibits the formation of thaumasite, and the breakdown of the calcium silicate hydrates, by maintaining a high pH.

In the main, frost resistance for mortar is implied on the basis of the compressive strength achieved at 28 days. Therefore the stronger the mortar, typically achieved through more cement, the more resistant the mortar will be. In reality this is a slightly flawed approach, as other "durability" aspects discussed here are adversely affected and thus frost resistance may be compromised if the mortar cracks and allows ingress of water.

It is therefore worth considering on what basis the frost resistance performance may be enhanced through the addition of lime, based on the known evidence from other construction products and materials.

As described for salt crystallization, in its simplest form, frost resistance is influenced by 2 fundamental opposing properties, the growth of ice crystals in the pore structure resulting in localised expansive forces and the tensile strength (restraining force) of that product or material.

It is known from ceramic products, that there is a critical pore size that is associated with frost resistance. Sánchez de Rojas et al [24] have identified that pores of $0.25-1.4~\mu m$ in diameter are thought to be critical to the frost resistance of clay roof tiles, and similar conclusions have been identified for clay bricks, blocks and pipes. It is thought that such pores fill with water by capillary uptake, but tend to retain the water. Pores of this size also tend to freeze at temperatures below freezing, thus the expansion of the ice crystals when formed is greater.

Larger pores tend not to be completely filled with water, therefore allowing some expansion capacity of the ice into an air gap in the pores.

In addition the connectivity of the very small pores within a material will often freeze before the pores themselves, therefore closing off the "pressure release" potential through this pathway.

As well as the pore size distribution, the chemical composition of the water itself can influence the development of the ice crystals. Water soluble salts are known to modify the freezing point of water, dependent upon their level of solubility. Due to the relatively low solubility of Ca(OH)₂ (1.85g/l), the impact of calcium hydroxide in solution in the pore water has minimal impact upon the freezing point, however chlorides and sulfates typically have greater solubility and thus have a greater impact upon the freezing point.

CONCLUSIONS

With the exception of rain penetration studies, much of the evidence for the benefits of lime additions into cement based mortars is circumstantial, though backed up by site based anecdotal evidence also. Few studies have been undertaken to investigate the causal linkages between the type and amount of lime in the mix, and the properties it modifies that result in better "durability" performance. Many of the statements made are therefore still theories and not fully proven, though many are based on fundamental and logical principles from other materials.

ACKNOWLEDGEMENTS

The authors would like to acknowledge support from the European Lime Association (EuLA) and its Member Companies for support for the production of this review paper.

REFERENCES

- 1. BRE. (1991) "Building Mortar". Digest 362, Building Research Establishment, UK.
- 2. Harrison, Gaze. (1989) "Laboratory scale tests on building mortars for durability and related properties." Masonry International Vol 3 No 1: p 35-41.
- 3. Sébaïbi, Dheilly, Beaudoin, Quéneudec. (2006) "The effect of various slaked limes on the microstructure of a lime-cement-sand mortar." Cement and Concrete Research 36: p971-978.
- 4. Arandigoyen, M., Alvarez, J.I. (2007) "Pore structure and mechanical properties of cement—lime mortars." Cement and Concrete Research 37: p767-775.
- 5. Zeng, Li, Fen-Chong, Dangla.(2012) "Effect of porosity on thermal expansion coefficient of cement pastes and mortars." Construction and Building Materials 28: p468-475.
- 6. Sickels Taves.(1995) "Elastic strain, creep and recovery in mortars; Additional analysis." Journal of Testing and Evaluation Vol 23: p377-383.
- 7. Mortar Industry Association. (2012) "The use of lime in mortar". Datsheet 18, MIA, UK. http://www.mortar.org.uk/documents/miadata18.pdf
- 8. Mosquera, Silva, Prieto, Ruiz-Herrera. (2006) "Addition of cement to lime based mortars: Effect on pore structure and vapot transport." Cement and Concrete Research 36: p1635-1642.
- 9. Wright, Wilkins, Johns. (1993) "Vairiables affecting the strength of masonry mortars." Masonry; Design and construction, problems and repair. ASTM STP 1180: p197-210.
- 10 Goodwin, West.(1980) "A review of the literature on brick/mortar bond." Technical Note 308, British Ceramic Research Association, Stoke on Trent, UK.
- 11 National Lime Association; (2000). "Lime bases mortars create watertight walls." Building Lime Group, National Lime Association, USA. http://www.lime.org/documents/publications/free downloads/lime-based mortars.pdf
- 12. Bowler, Jackson, Monk.(1996) "The role of mortar workability (cohesivity) in the rain penetration of masonry." Masonry International Vol 10 No 1: p24-25.
- 13. Bowler, Sharp.(1998) "Testing of various brick-mortar combinations for mortar durability, efflorescence potential and resistance to rain penetration." Proceedings of the 5th International Masonry Conference. p31-36.
- 14. Colantuono, Dal Vecchio, Marina, Mascolo and Vitale.(1996) "Cement-lime mortars joining porous stones of masonries able to stop capillary rise of water." Cement and Concrete Research, Vol. 26,: p861-868.
- 15. West, Ford, Peake.(1976) "The effect of suction rate of bricks on the permeability of mortar." Technical Note 254, British Ceramic Research Association, Stoke on Trent, UK.
- 16. Lubelli., van Hees., Huinink., Groot.(2006) "Irreversible dilation of NaCl contaminated lime-cement mortar due to crystallization cycles." Cement and Concrete Research 36: p678 687.
- 17. Lubelli, van Hees, Groot. (2004) "The role of sea salts in the occurrence of different damage mechanisms and decay patterns on brick masonry." Construction and Building Materials 18: p119-124.
- 18. Gaze, Crammond. (2000) "The formation of thaumasite in a cement:lime:sand mortar exposed to cold magnesium and potassium sulfate solutions." Cement & Concrete Composites 22: p209-222.
- 19. CEN (2011) "EN 771-1 Specification for masonry units Part 1: Clay masonry units"

- 20. CEN (2006) "TS 772-22 Methods of test for masonry units Part 22 Determination of freeze thaw resistance of clay masonry units."
- 21. CEN (2010) "EN 998-2 Specification for mortar for masonry Part 2: Masonry mortar".
- 22. Givens. (1995) "Field testing of masonry mortars for durability." Proceedings of the British Masonry Society. p19-26.
- 23. Bowler. (1993) "Deterioration of mortar by chemical and physical action." Masonry International, Vol 6 No 3: p78-82.
- 24. Sánchez de Rojas, M.I., Marín, F.P., Frías, M., Valenzuela, E., Rodríguez, O. (2011) "Influence of freezing test methods, composition and microstructure on frost durability assessment of clay roofing tiles." Construction and Building Materials, 25, p2888-2897