“Green”, non-corrosive de-icers: A remedy for concrete bridge corrosion, but can they harm the paste?

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ABSTRACT: This paper forms part of an ongoing research concerning the feasibility, viability and cost-effectiveness of the adoption of an alternative method of winter de-icing operations for highway bridges, based on the use of novel, non-corrosive de-icing chemicals as replacement for rock salt. The University of Surrey and Anglia Ruskin University in the UK are currently evaluating the effects of solutions of two such de-icers, namely Calcium Magnesium Acetate (CMA) and Sodium Acetate (NAAC), on the microstructure and the properties of cement paste. The results presented in this paper were derived using SEM imaging and element mapping in order to identify possible changes in the cement paste resulting from contact with these alternative de-icers. Preliminary results of the microscopy investigation of one year specimens has indicated that the CMA solutions produces minor changes in the surface layers of the paste. Further work concerning the effects of the CMA solutions on the physical properties of the hardened cement paste is in progress to ascertain the significance of the observed changes.

KEYWORDS Alternative De-icing Salts, Durability, Brucite, Decalcification.

1 INTRODUCTION

De-icing and anti-icing products have been used for decades on highways especially in countries experiencing prolonged periods of snowfall during the winter. Chloride-based products and principally rock salt have always been the most popular ones due to their effectiveness, ease of storage and application and low cost (TRB 1991). However, over the last few decades, the construction industry has been faced by severe and costly maintenance issues some of which are the consequence of the repeated utilisation of such agents. The adverse (corrosive) effect of chloride-based chemicals on the life cycle of reinforced concrete bridges and parking structures (Pullar-Strecker 2002, Richardson 2002) has raised concerns with respect to the sustainability of current de-icing practices.

Globally, several structural surveys carried out in different countries have revealed that the direct cost of maintaining, repairing and replacing deficient bridge structures amounts to a significant part of the Gross Domestic Product of many developed countries. Figure 1 below provides indicative figures of such costs reported for the USA, the UK and Japan. These figures do not include costs inflicted by damage on roadside objects, vehicle and loss of floral species. Moreover, indirect costs due to traffic delays and loss of productivity have been estimated to reach over ten times the direct cost of maintenance, repair and replacement (TRB 1991).

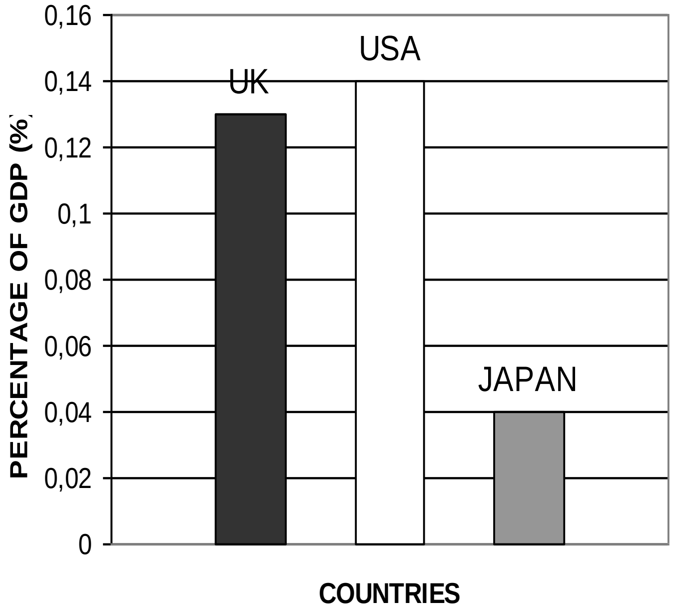


Figure 1. Costs of repair of corrosion damaged bridges, expressed as percentages of the GDP for UK, USA and Japan.

The recognition of the negative effects of de-icing chemicals combined with the necessity for their use has led construction professionals and academics to come up with innovative ways to protect reinforced concrete structures prone to corrosion. Part of the solution has been focused on adopting alternative approaches towards winter operations by the use of environmentally friendly de-icing chemicals. Most of the data comes from the US where a number of pilot projects were commissioned by the US Federal Highways Agency, in order to evaluate the effectiveness of alternate de-icers in reducing rebar corrosion. One of the most widely investigated alternative de-icers is Calcium Magnesium Acetate (CMA) which is produced by reacting dolomitic lime with acetic acid. This chemical has been demonstrated by many researchers to be no more corrosive than water on embedded reinforcement and metal roadside objects (Kennelley & Locke 1990, McCrum 1988, McCrum 1989, Miller 1992, Miller 1993, Slick 1988, TRB 1991). CMA has been investigated for its corrosiveness towards various metals including reinforcing steel, its environmental impact, its effects on concrete and other aspects. Although it seems to be a safe option in many respects, its most significant drawback is its high cost of production which ranges between 20 to 30 times the cost of rock salt. Other more cost-effective methods of production have been identified but are still at the stage of investigation. A report carried out following a request by the US congress identified the benefits which could arise from the replacement of rock salt by CMA but at the same time highlighted that it is doubtful whether a complete substitution would provide the expected financial benefits due to its high cost of production but also due to insufficient data regarding the long-term effects.

2 MAIN OBJECTIVES

The work presented in this paper aims to identify possible damage or alteration in the microstructure of the cement paste of normal concrete mixes in contact with CMA solutions and to determine the depth from the exposed surface of the paste at which changes take place.

3 BACKGROUND

Several studies have been carried out over the past two decades to ascertain the effects of CMA de-icers on the properties of concrete. In some cases, contradictory results have been recorded for similar kinds of tests by different researchers, which is mainly due to the diversity of conditions under which those experiments were undertaken. This seem to suggest that CMA can act very differently when in contact with concrete depending on factors such as ambient temperature, Ca/Mg molar ratio of the CMA, concentration of the CMA solution, concrete mix design, cement composition, presence of admixtures, type of aggregates etc. In this perspective, the results from various studies are not directly comparable. Nonetheless, they do offer an indication of the mechanism that governs the changes, which take place in the concrete microstructure as well as in the composition of the CMA solution.

Cody et al. (1996), who carried out a study on the effects of Magnesium and Calcium de-icers, but not CMA, speculate that the latter, if used as a substitute for rock salt de-icers in the context of reinforcement corrosion prevention, may have unintended consequences in accelerating concrete deterioration. The study concerned aged concrete cores from highways of known service records in contact with NaCl, CaCl, $MgCl_2$ and Mg $(CH_3CO_2)_2$. The authors conclude that $MgCl_2$ solutions are the ones that caused the most severe deterioration in concrete and they attribute this chiefly to the formation of magnesium silicate hydrates, MSH, produced by the reaction of dissolved magnesium in the pore solution with calcium silicate hydrates, CSH. MSH is non-cohesive and therefore, associated with the lack of cementitious properties of the cement paste.

This view is backed by Santhanam et al. (2001) whose paper reports the results of an investigation on the effects of magnesium sulphate solutions on the expansion and microstructure of different types of Portland cement mortars. Their research focused on the role of magnesium in the mechanism of sulphate attack when the attacking solution contains magnesium ions. Their studies suggested that a layer of brucite (magnesium hydroxide) forms on the surface almost immediately after the introduction of the specimens into the solution. It is also reported that this layer provides a barrier to the free passage of the external solution. Gypsum and ettringite seem to have formed underneath this barrier and in close proximity to the surface of the specimens. In areas where the brucite barrier is broken down due to high disintegration of the samples, decalcification of the calcium silicate hydrate (CSH), and its conversion to non-cementitious magnesium silicate hydrate (MSH), after prolonged exposure to the solution, takes place and causes the ultimate failure of the specimens. However, the authors do not record the expansive action of the brucite itself as being responsible for any part of the deterioration of the mortar samples. The relevance of this study to the current report is obvious and hinges on the fact that it concerns the effect of solutions containing magnesium ions, on concrete.

Moreover, Peterson (1995) has found that mortar samples immersed in CMA solutions tend to expand continuously over a period of 6 months. In addition, this study notes that the magnitude of the expansion increases with an increase in the Ca/Mg molar ratio of the CMA, the W/C ratio of the mix and the ambient temperature. Therefore, the author speculates the formation of a double salt composed by calcium hydroxide and calcium acetate which causes the expansion. This is more so in samples with greater W/C ratio and thus, greater pore volume to facilitate such a salt. This study, also recognises the formation of a thin layer of brucite on the surface of the samples which, according to the author precipitates as calcium hydroxide leaches out of the samples into the solution therefore, increasing the CMA solution's Ca/Mg ratio and its pH. The same study also concludes that a higher content of magnesium ions in the CMA solution accelerates the dissolution of the hardened cement paste and reduces its strength further. The author attributes this effects to the fact that the combined reactions of brucite formation on the surface of the samples and leaching of calcium hydroxide greatly increases the solution's content of Ca ions and therefore renders it harmful towards the hardened paste.

Also Santagata and Colepardi (2000) suggest leaching of calcium hydroxide which they back with the evidence that when pozzolanas are used, the strength is not greatly impaired due to the fact that calcium hydroxide gets rapidly consumed by the pozzolanic materials.

4 MATERIALS

4.1 *Cement composition*

The composition of the raw materials employed for the cement used in this investigation is outlined in Table 1 below.

Table 1. Composition of raw materials employed for cement

Oxide	Percentage (%)
SiO_2	20.62
Al_2O_3	5.02
Fe_2O_3	2.50
CaO	65.24
MgO	1.11
SO_3	2.85
K_2O	0.56
Na_2O	0.20
$EqNa_2O$	0.57
FCaO	0.86
L.O.I.	1.20

4.2 *Immersion solutions*

The test samples were immersed in a CMA solution at a concentration of 6.181% which was chosen as it achieves the same freezing point as a 3.5% NaCl solution, used as a control in this investigation.

5 EXPERIMENTAL DETAILS

5.1 *Scanning electron microscope imaging*

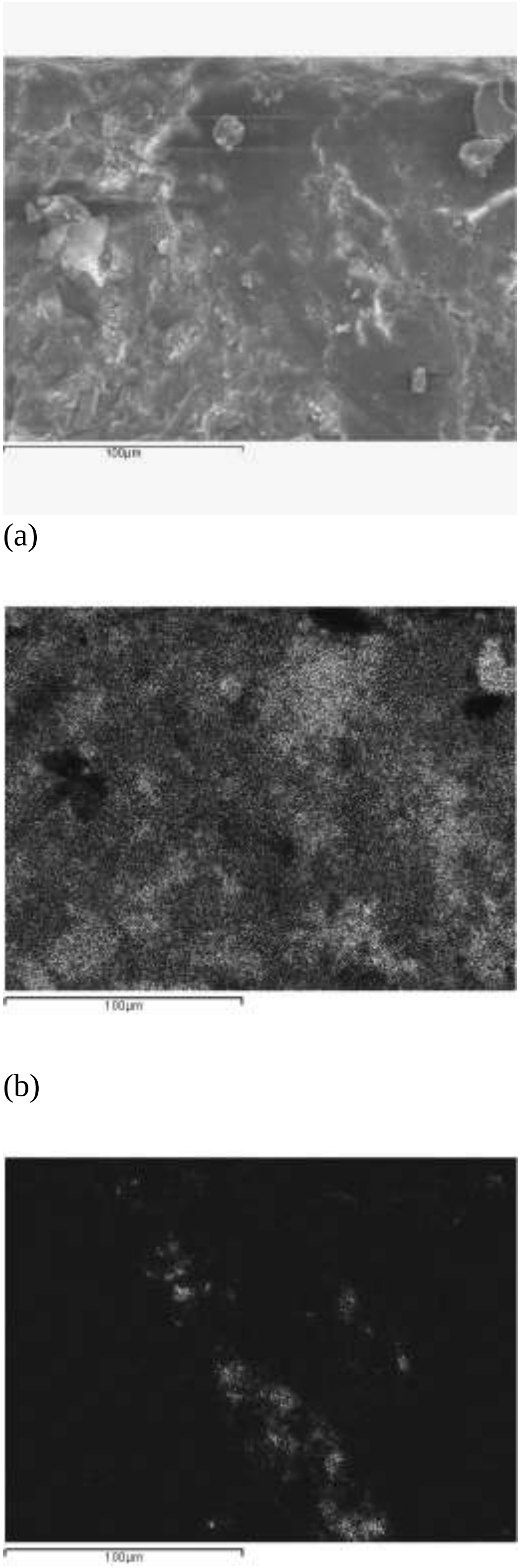
Small cement paste prisms (10 mm x 10 mm x 110 mm), were cast with a water/cement ratio of 0.4 and were immediately placed in the curing room at 100% RH. They were then de-moulded the following day and were placed back in the curing room for a further 27 days. After curing, the samples were transferred to a room with constant temperature and relative humidity (20˚C and 70% RH), where they remained for the rest of the experimental process. They were then coated with resin and left to dry overnight. The coating process was repeated the following day and they were, again, left to dry overnight. The following day the hardened resin along with the as-cast surface was removed from one of the two smaller faces of the sample, with a diamond saw. This way, it was ensured that the penetration of the de-icer solution from that contact face would be unidirectional so that the depth of penetration could be estimated with higher precision. Moreover, the removal of the as-cast surface of that particular face ensured that misinterpretations due to contamination would be avoided. The immersion regime which the samples underwent involved two-weekly cycles (one week immersed in solution and one week dry). Although wet-dry cycles may bear no particular significance in this case, the experiment was designed to correlate with the ponding regime performed on miniature slab samples designed for reinforcement corrosion testing, which forms the main core of this general project.

The effect of the immersion process was microscopically examined at predetermined times for a duration of 1 year after the end of the curing process, namely at 28 days, 90 days, 6 months and 1 year. The examination was performed with the help of a HITACHI 3200 scanning electron microscope. Specifically, the samples were cut in the middle with a diamond saw along their longitudinal axis which, contrary to thin slicing, allows for visualisation of the effects of the solutions on the same sample, simply by moving the cut profile under the microscope. Samples were carbon coated before they were viewed in the SEM. Different images were taken at various locations, at different depths from the surface of the exposed face and at different magnifications, which varied from x300 to x9000. Element mapping was performed with the help of the microscope in order to help identify the elements and compound formations at locations of interest.

6 RESULTS AND DISCUSSION

6.1 *General*

The images and element maps presented in this section are of a magnification of x600 and x300 where the x600 images cannot facilitate the whole of the areas of interest where changes are taking place and they represent the top part of cut profiles as described above in section 5. Thus, the surface of the sample in each image lies at the top of the picture. Images were taken for samples in a 6.181% CMA solution, at 4 different times after the end of curing, namely at 28 days, 3 months, 6 months, 1 year. The element maps presented here are the ones for Ca and Mg as they are more critical in drawing conclusions for the purposes of this paper.

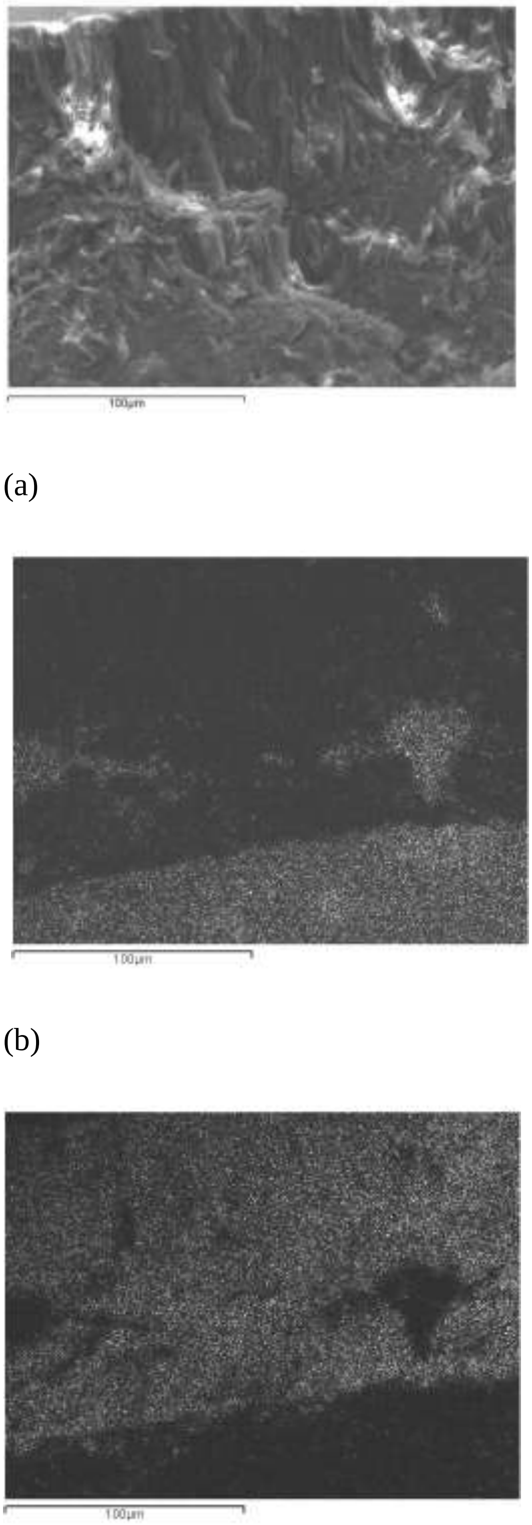


(a)

(b)

(c)

Figure 2. Profile image and corresponding element maps for sample subject to the immersion regime for 28 days at a magnification of x600. (a) profile image, (b) Ca map, (c) Mg map.



(a)

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Figure 3. Profile image and corresponding element maps for sample subject to the immersion regime for 3 months at a magnification of x600. (a) profile image, (b) Ca map, (c) Mg map.

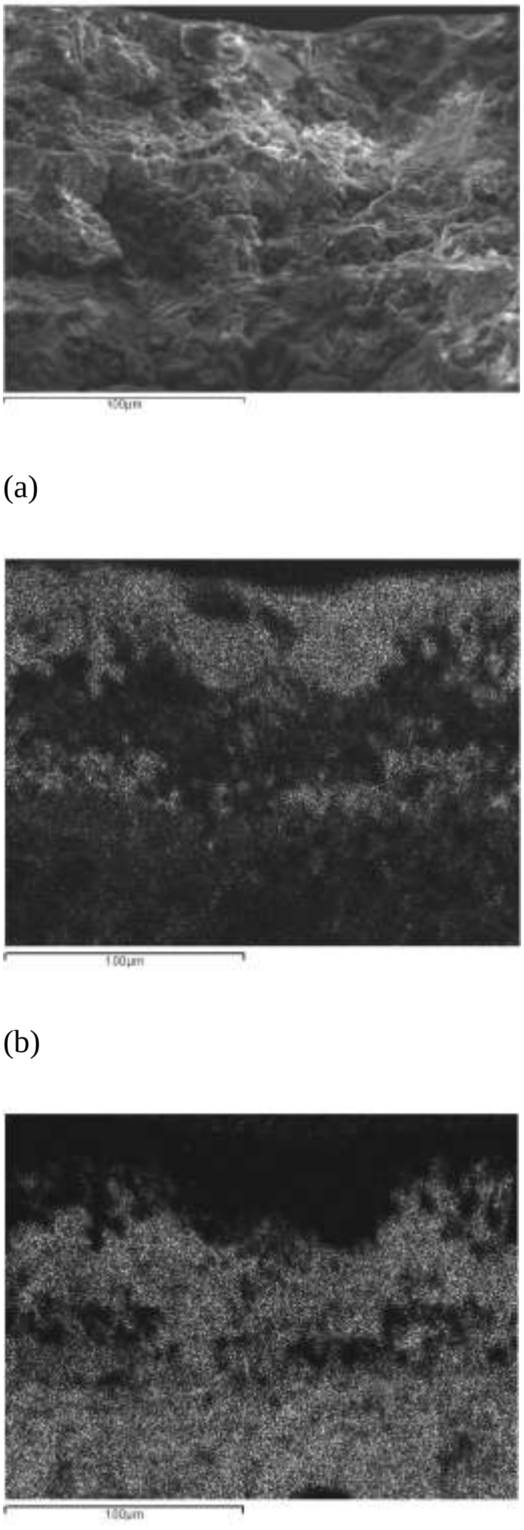


Figure 4. Profile image and corresponding element maps for sample subject to the immersion regime for 6 months at a magnification of x600. (a) profile image, (b) Ca map, (c) Mg map.

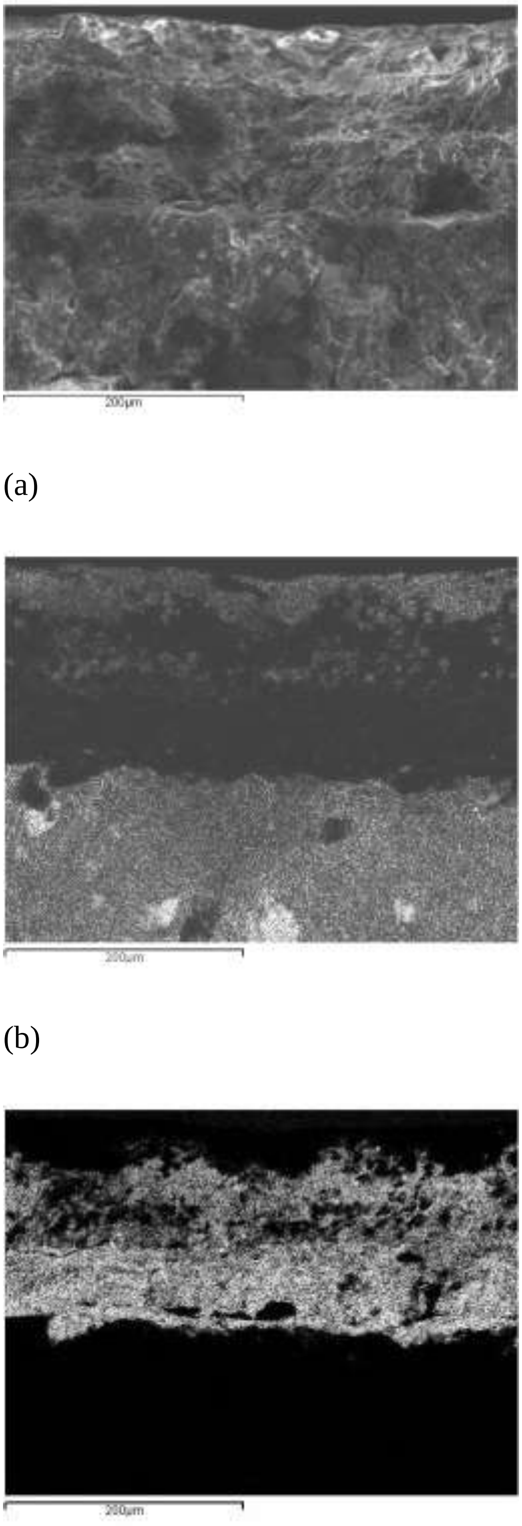
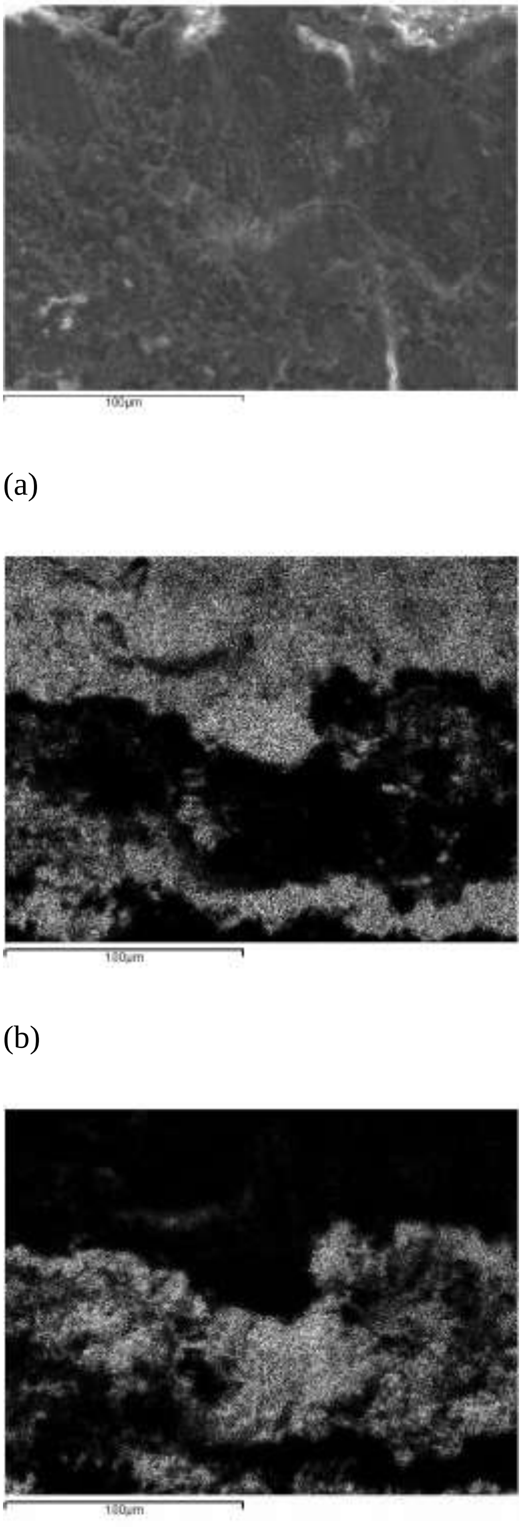


Figure 5. Profile image and corresponding element maps for sample subject to the immersion regime for 6 months at a magnification of x300. (a) profile image, (b) Ca map, (c) Mg map.

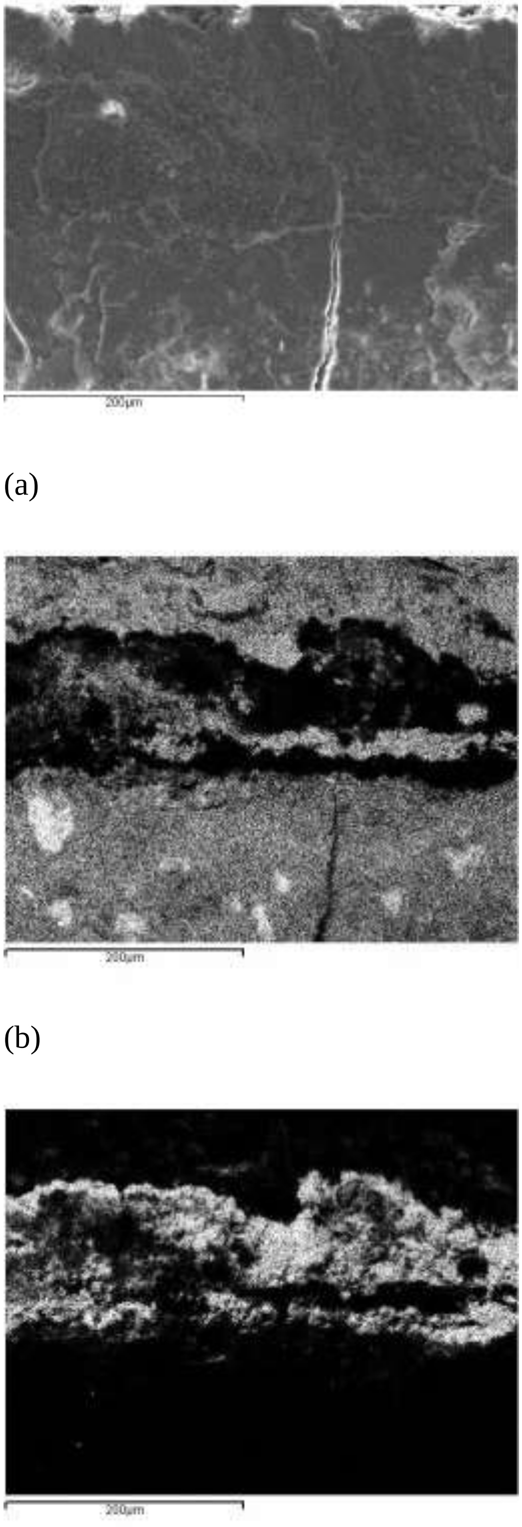


(a)

(b)

(c)

Figure 6. Profile image and corresponding element maps for sample subject to the immersion regime for 1 year at a magnification of x600. (a) profile image, (b) Ca map, (c) Mg map.

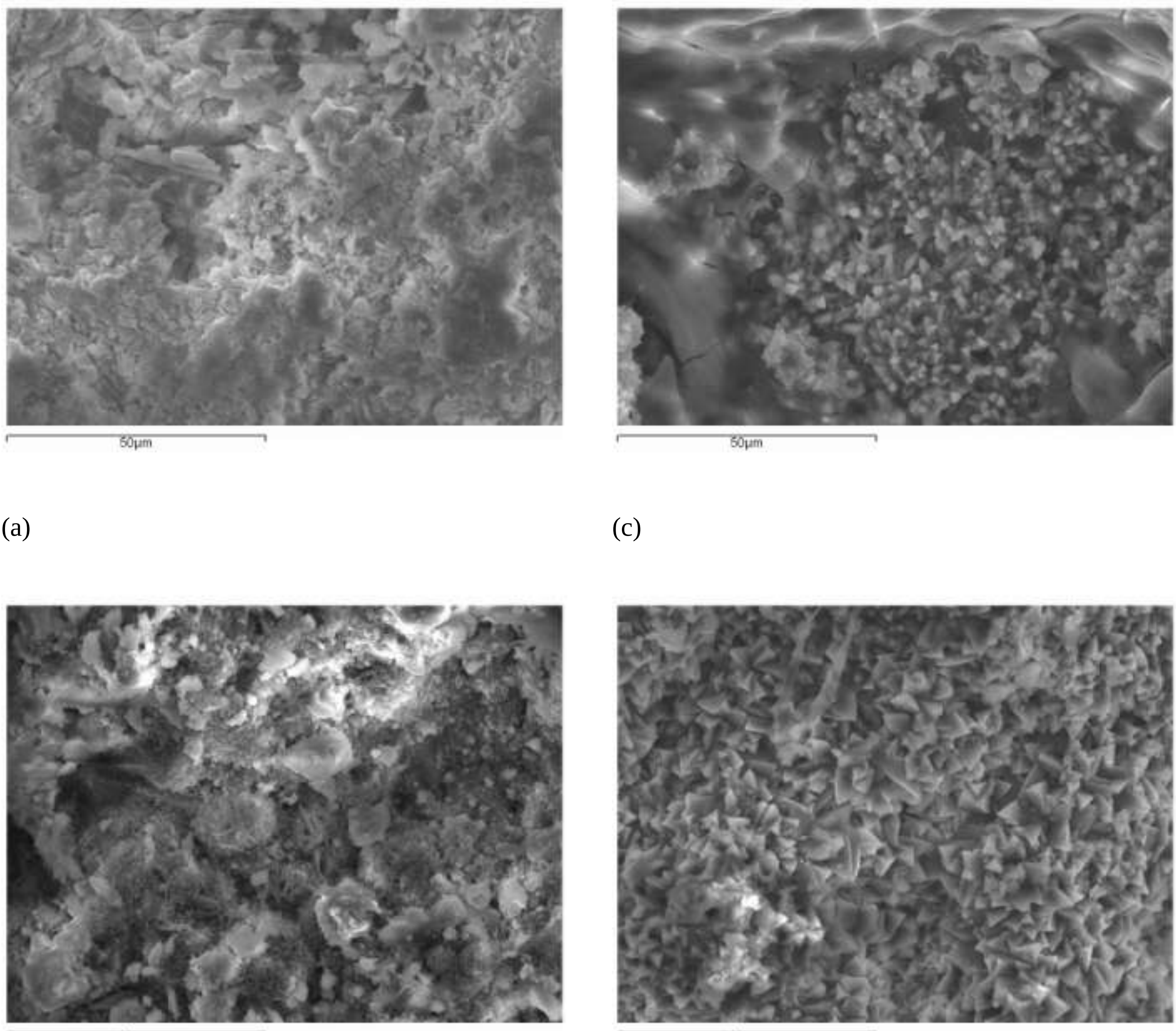


(a)

(b)

(c)

Figure 7. Profile image and corresponding element maps for sample subject to the immersion regime for 1 year at a magnification of x300. (a) profile image, (b) Ca map, (c) Mg map.



(a)

(c)

(b)

(d)

Figure 8. SEM images of the exposed face of cement paste samples at different times during immersion in a 6.181% CMA solution at a magnification of x1200. (a) 28 days, (b) 3 months, (c) 6 months, (d) 1 year.

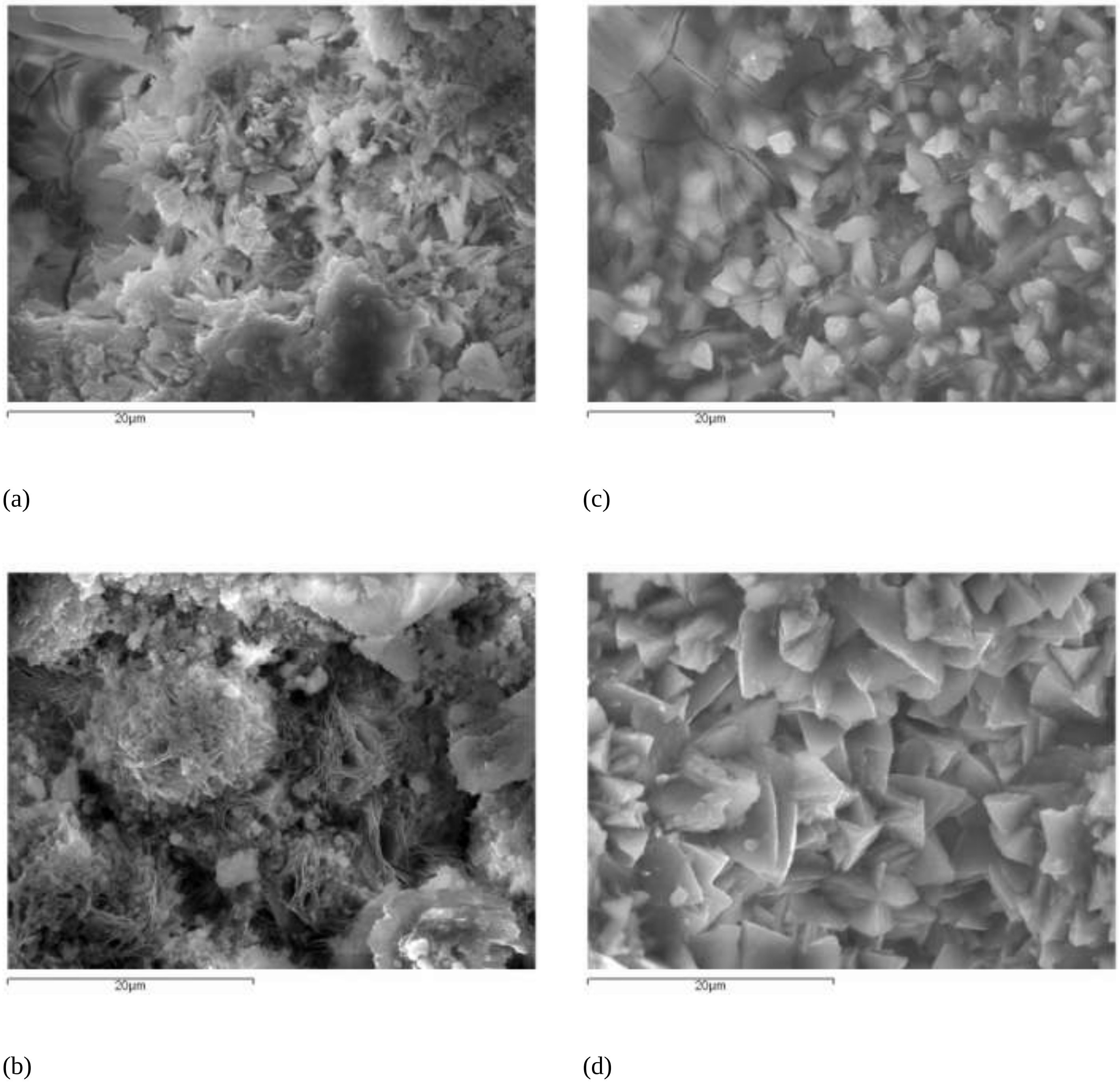


Figure 9. SEM images of the exposed face of cement paste samples at different times during immersion in a 6.181% CMA solution at a magnification of x3000. (a)28 days, (b)3 months, (c)6 months, (d) 1 year.

6.2 *Discussion on images and element maps*

In Figure 2 below, it seems that after the first 28 days of the immersion regime described in section 5, no visible changes have taken place. No replacement of calcium with magnesium can be detected at the top layers and no signs of calcium hydroxide leaching are obvious. This can be confirmed by visual inspection of the microscopic images of Figures 8a, 9a where some fibrous $CaCO_3$ crystals along with amorphous CSH can be observed but no crystals arising from the contact of the sample with the CMA solution can be seen.

As it can be seen in Figure 3, however, after 3 months of the immersion process, the first 200 μm on the exposed surface of the sample are occupied by a compound containing magnesium which is most likely magnesium hydroxide (brucite) as supported by the relevant existing literature. Brucite, which is insoluble, provides a relatively impermeable layer which inhibits substantially the passage of other ions from the solution towards the paste. Its crystal is an octahedron made up by several layers of sheets which are loosely held together, thus opening up with time, to form a rosette-like structure as the ones which can be seen in the images of Figures 8b, 9b. Despite the fact that it is an expansive compound, it is unlikely to be able to damage the hardened paste as it seems to be occurring in the form of deposits on top of the initial surface of the samples. It precipitates as a result of a combination of factors; as calcium hydroxide leaches it increases the pH of the surrounding solution. When the pH reaches a value of about 9, Magnesium acetate becomes unstable losing magnesium ions and therefore precipitating on the surface as brucite, by means of the following equation:

$$Mg^{2+} + Ca(OH)_2 + Mg(OH)_2 + Ca^{2+}$$

The liberated calcium ions make the surrounding solution contain more and more calcium acetate.

After 6 months of the immersion process, as it can be seen in Figures 4-5, a 50 μm thick layer of calcium-containing compounds has formed on top of the brucite layer. This can be a combination of compounds including calcium hydroxide, calcium carbonate and compounds arising from the contact of leaching calcium hydroxide and the calcium acetate in the solution . Since there is not enough calcium hydroxide leaching out at this stage both because of availability and also because of the relatively impermeable overlying layer of brucite, the magnesium acetate in the surrounding solution does not lose magnesium ions any more. Therefore, as mentioned above this new layer of calcium-containing compounds is facilitated among the loosely held sheets of the rosette-like crystals of brucite, as it can be seen in Figures 8c, 9c. Since these new compounds can be expansive according to the existing literature (Cody et al. 1995), they could create cracks in the brucite layer thus, facilitating the intrusion of magnesium ions deeper in the cement paste, and the formation of the non-cementitious MSH which could replace the CSH therefore dramatically reducing the strength of the hardened paste.

After the samples have undergone a year of the immersion regime employed in this investigation, the top layer of the calcium-containing compounds has become only slightly thicker (Figs 6-7) which is an indication of the retarding role of the impermeable brucite layer. Figures 8d, 9d indicate that the only thing present on the surface of the exposed face after a year is calcium-containing compounds. However, after a year, apart from what are essentially deposits, there don’t seem to be any changes deep within the hardened cement paste.

7 CONCLUSIONS

It seems that after a year of immersion cycles, no significant changes have taken place deep inside the hardened paste of the samples employed in this investigation. What becomes obvious is the brucite layer which precipitates on the surface in contact with the CMA solution. Its effect seems to be beneficial to the paste rather than detrimental. It forms at a time between 28 days and three months of this type of immersion cycles and it seems to inhibit ion transport in and out of the paste. An additional layer of calcium-containing compounds forms on top of this brucite layer at some point between 3 and 6 months, which could further limit transport of ions between the paste and the surrounding solution. However, it is possible that these calcium-containing compounds could, through their expansion, break down the brucite layer, and therefore facilitate the passage of magnesium and other ions into the sample and thus the formation of MSH which lacks cementitious properties. However, it becomes abundantly clear that these results need to be correlated to physical property tests. Moreover, continuation of these tests for a longer period of time could provide a clearer picture on whether CMA could indeed be harmful to the paste in the long term.

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