

Sodium Acetate: An Overlooked, “Green” De-icing Solution for Highways

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ABSTRACT

This study investigates sodium acetate [NAAC], a rather neglected bio-degradable de-icer, which may, however, present a viable solution towards sustainable and environment-friendly winter operations in certain situations. The results presented here are a selection of data obtained by SEM imaging and element mapping, together with X-Ray diffractometry in order to demonstrate the benign nature of NAAC solutions with regard to their interaction with cement pastes. The effect of the inclusion of microsilica in the cement paste in these tests is evaluated through the use of pure OPC and microsilica containing specimens. The results obtained suggest that sodium acetate is an effective de-icer that may deserve as much attention by researchers and the industry, in the same way as other well known alternative de-icers

INTRODUCTION

In June 2009, the Institution of Civil Engineers [ICE] launched a report on infrastructure resilience in the UK [Institution of Civil Engineers 2009]. During the launch, ICE president Jean Venables was quoted saying “Neglecting our critical infrastructure could result in major damage to our economy, environment and at the very worst, loss of life” [NCE 2009]. The report, only highlighted the fact that over the last few decades, the infrastructure in the UK and other developed nations has been facing severe and costly maintenance problems, a large percentage of which concerns the deterioration of highway bridges and multi-storey parking buildings. The main factor contributing to the damage of these valuable assets is the corrosive effect of chloride-based chemicals used for ice-melting in winter operations [Pullar-Strecker 2002;Richardson 2002]. Chloride de-icers and mainly rock salt have been the most widely used agents world-wide, due to their low cost and ease of application [TRB 1991]. However, the long term damage they produce through corrosion of steelwork and concrete reinforcement, may dwarf short term economic benefits.

As an indication, the cost of corrosion solely in the construction sector in the UK has been estimated around £2.5 billion [PRA 2003], while costs for repair and rehabilitation of highway bridges in the same country has been estimated to be in the range of £616.5 million [Wallbank 1989]. This expenditure would amount to about 0.13% of the GDP of the UK [Office for National Statistics 2005]. Several surveys carried out in different countries have revealed that the cost of maintaining, repairing and replacing deficient bridge structures amounts to similarly significant percentages of their Gross Domestic Product [JACC 1999;TRB 1991]. Such figures do not include damage on roadside objects, vehicles, loss of floral and faunal species, surface water quality, the adverse effects on soil structure and the migration of sodium and chloride ions into water supplies [TRB 1991], traffic delays and subsequent lost productivity as well as funds allocated for the planning and scheduling of the repair and rehabilitation strategies. It is, estimated that indirect costs can amount to ten times the value of direct costs [Koch et al. 2002;TRB 1991].

The negative effects of chloride de-icers did not go unnoticed by academics and construction professionals who have sought innovative ways to protect corrosion-prone concrete structures. Apart from designing for durability, part of the focus of relevant research has been on alternative, non-corrosive de-icing chemicals. A “family” of de-icers that could potentially fulfil this demand are the acetate-based de-icers. The US Federal Highways Agency, identified Calcium Magnesium Acetate [CMA] as a possible alternative to rock salt and subsequently funded a number of projects to evaluate it, in terms of its ice-melting effectiveness and effects on structures [Kennelley & Locke 1990;Locke & Boren 1987;McCrum 1988;McCrum 1989;Miller 1993;Slick 1988;TRB 1991]. 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.

However, sodium acetate, another commercially available de-icer, which is currently used on airport runways and few urban roads and highways at locations experiencing prolonged winters, may have been overlooked. Literature on the effects of sodium acetate on building materials is very scarce, as the weight of research was placed on CMA.

MAIN OBJECTIVES

The work presented in this paper aims to identify possible effects, if any, on the microstructure of OPC and microsilica containing cement paste in contact with NAAC solutions and to determine the depth from the exposed surface of the paste at which changes, if any, take place.

BACKGROUND

As mentioned above after recognition of the potential benefits of acetate-based de-icers [TRB 1991], funding became available in the USA for research almost exclusively into CMA, while other acetate de-icers including sodium acetate seem to have been neglected. This may have also possibly been due to some early environmental concerns [Fischel 2001]. Despite concerns about Biological Oxygen Demand (BOD) and Dissolved Oxygen (DO) levels of receiving waters practical experience in Aspen and Snowmass, Colorado, USA, has recorded no adverse effects [The City of Aspen 2002a;The City of Aspen 2002b].

Regarding the ice-melting performance of sodium acetate, Table 1 displays its eutectic and effective temperatures against those of sodium chloride and CMA. The effective temperatures are the lowest temperatures that these chemicals have been observed to effectively melt ice under real conditions. It becomes obvious that the effective temperature of sodium acetate is much lower than that of the other two chemicals due to the fact that it possesses exothermic properties.

Table 1. Eutectic and Effective Temperatures of selected de-icers [CRC Press 2000; Mangold 2004]

DE-ICER	Eutectic Concentration (%)	Eutectic Temperature (C°)	Effective Temperature (C°)
CMA	32.60	-27.78	-6.67
NAAC	27.00	-21.67	-15.00
Sodium Chloride	23.00	-21.12	-9.44

In the UK, a study conducted in 2005, in order to evaluate the effectiveness of acetate de-icers, concluded that the recommended application rates' ranges are, according to the authors, 20-40g/m² for CMA, 15-25g/m² for NAAC and 10-40 g/m² for rock salt. The finding that less NAAC is required than CMA to achieve comparable results is in line with the NAAC's lower eutectic concentration and lower effective temperature reported in Table 1.

MATERIALS

Cement composition

The cement composition used in this study is shown in Table 2, below.

Table 2. Composition of cement used

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	EqNa ₂ O	F	CaO	L.O.I.
(%)	20.62	5.02	2.50	65.24	1.11	2.85	0.56	0.20	0.57	0.86	1.20	

The sodium acetate used was the commercially available NAAC produced by Cryotech which contains less than 1% b.w. a phosphorus-based corrosion inhibitor.

Scanning Electron Microscope imaging

The prisms were immersed in a NAAC solution with a concentration of 4.367% b.w., which was chosen as it demonstrates the same freezing point as a 3.5% b.w. NaCl solution, which approximates the concentration of NaCl in seawater and was arbitrarily used as a control in this general project.

EXPERIMENTAL DETAILS

Exposure regime

Cement paste prisms (10 mm x 10 mm x 110 mm), with a 0.4 w/c ratio were cast and then placed in the curing room at 20°C. The following day they were de-moulded before being placed back in the curing room for a further 27 days. After the completion of curing, they were placed in a space with a temperature of 20°C and 70% relative humidity. The prisms underwent the exposure to the chemicals under examination in this temperature and relative humidity. Specimens intended for SEM imaging were then coated with two coats of resin. The hardened resin together with the as-cast surface was removed from one of the two smaller faces of the prism, with a diamond saw to make sure that the flow of the de-icer solution from that contact face would be unidirectional so that the depth of possible effects on the paste could be estimated with higher precision. Specimens for X-Ray diffraction tests were not coated. The exposure regime of the specimens involved two-weekly cycles (one week immersed in solution and one week dry). The wet-dry cycles were designed to provide correlation with the ponding regime performed on slab specimens designed for rebar corrosion testing, which was part of this general study.

Scanning Electron Microscope imaging

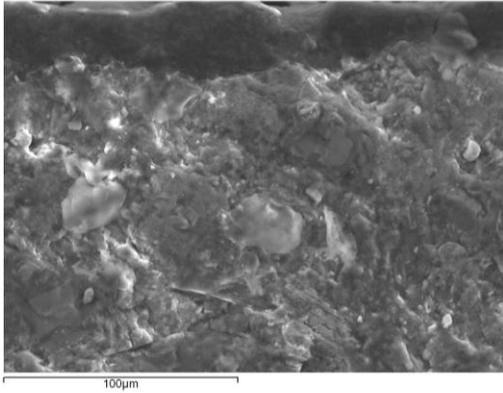
The effect of the immersion process was microscopically examined at 1 year after the end of the curing process,. The examination was performed with a HITACHI 3200 SEM. The specimens were cut along the centre of their longitudinal axis, which allowed visualisation of the effects of the solutions on the cut profile. Samples were carbon coated before they were viewed in the SEM. Element maps were taken with the microscope in order to identify the elements and possible compound formations.

X-Ray diffractometry

In the case of the XRD spectrometry tests, just before testing, the specimens were ground using mortar and pestle and passed through a 50µm sieve. When adequate quantity of at least 1g of ground sample was collected, it was sprayed with acetone to remove any water or moisture still present in the fine powder. When the acetone evaporated, the sample was immediately taken for testing to avoid carbonation. In order to identify phases present in small quantities, in surface layers, the surface of separate specimens was scraped using a razor blade, taking extra care to ensure fineness of the resulting powder. Although the final quantity of material collected in this manner was usually small, it was mounted on special backing plates, which allowed the thin layer of powder to be analysed by the diffractometer. Powder samples were mounted on a special plate. The top surface of the sample was then pressed flat at the same level as the top surface of the plate and any excess powder was removed with a brush. The plate was, in turn, inserted into the diffractometer. The cabin door was then properly locked and data was acquired with the help of a computer and specialised software X'Pert Data Collector by Panalytical. The diffractometer used in this study was the Panalytical X'Pert Pro. Measurements were between 2θ angles of 10 to 60 and the 2θ step size of the scan was 0.017. Each scan lasted eight minutes. X-ray diffraction spectrometry test results presented in this paper are the ones taken at 1 year after the end of curing. The data was analysed with the help of the X'pert Highscore software by Panalytical. The results were used for correlation with the findings of the SEM investigation.

RESULTS

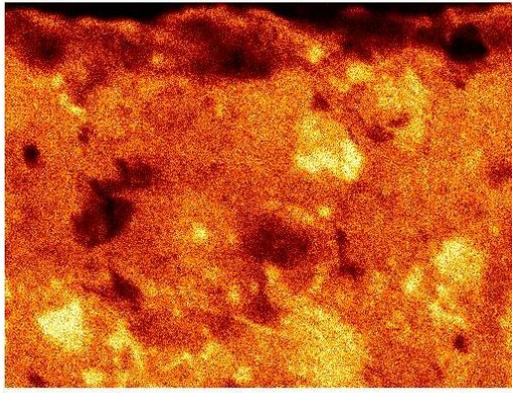
The SEM images and element maps presented are of a x1200 magnification. and they represent the top part of cut profiles as described above. Thus, the exposed surface of the sample is at the top of the picture. XRD curves and derived matched phases are also presented in this section.



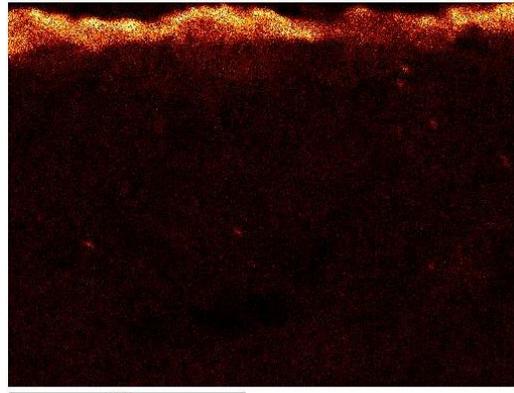
SEM image



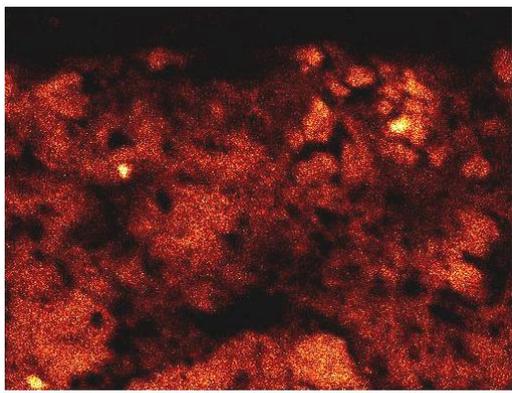
Sodium map



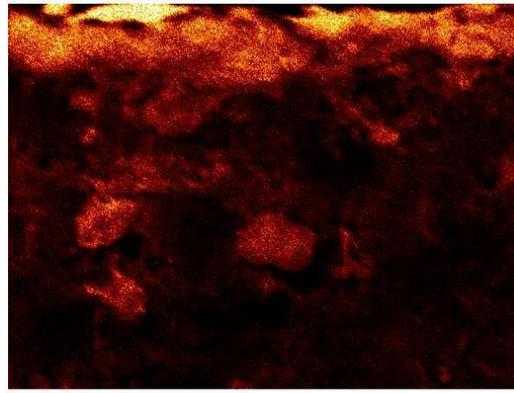
Calcium map



Phosphorus map

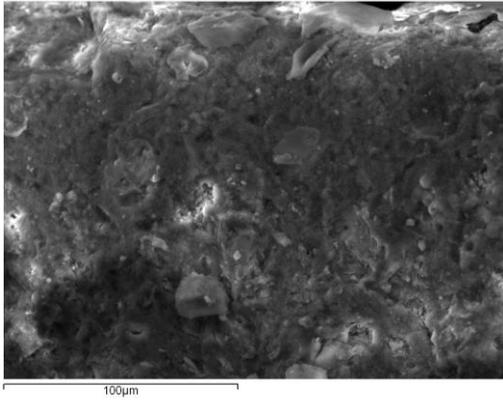


Silicon map

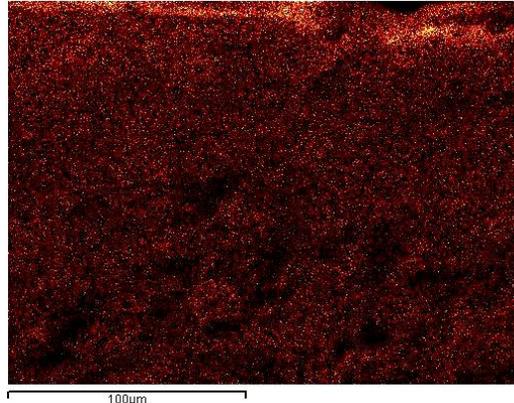


Carbon map

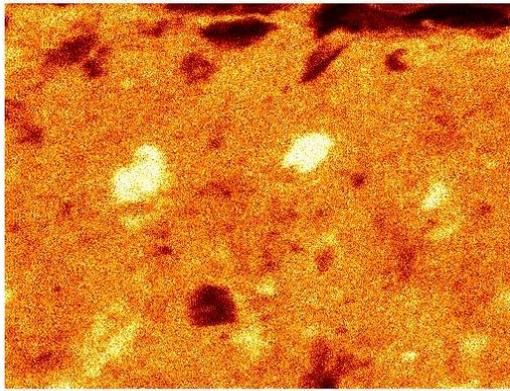
Fig. 1. SEM image and element maps for OPC specimens after one year of exposure



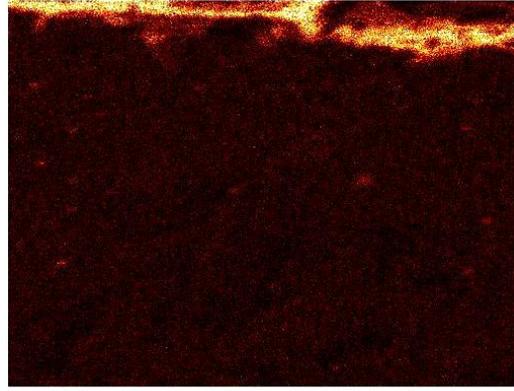
SEM image



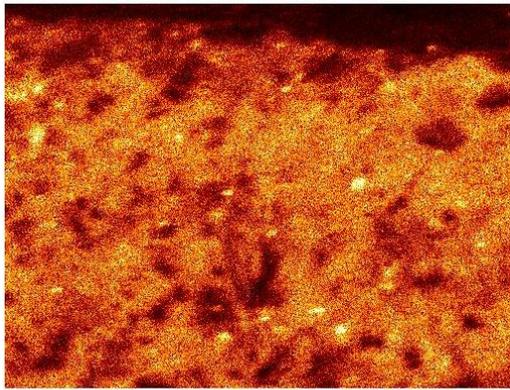
Sodium map



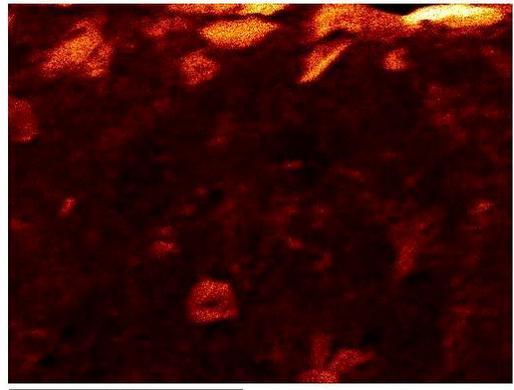
Calcium map



Phosphorus map



Silicon map



Carbon map

Fig. 2. SEM image and element maps for 90% OPC / 10% Microsilica specimens after one year of exposure

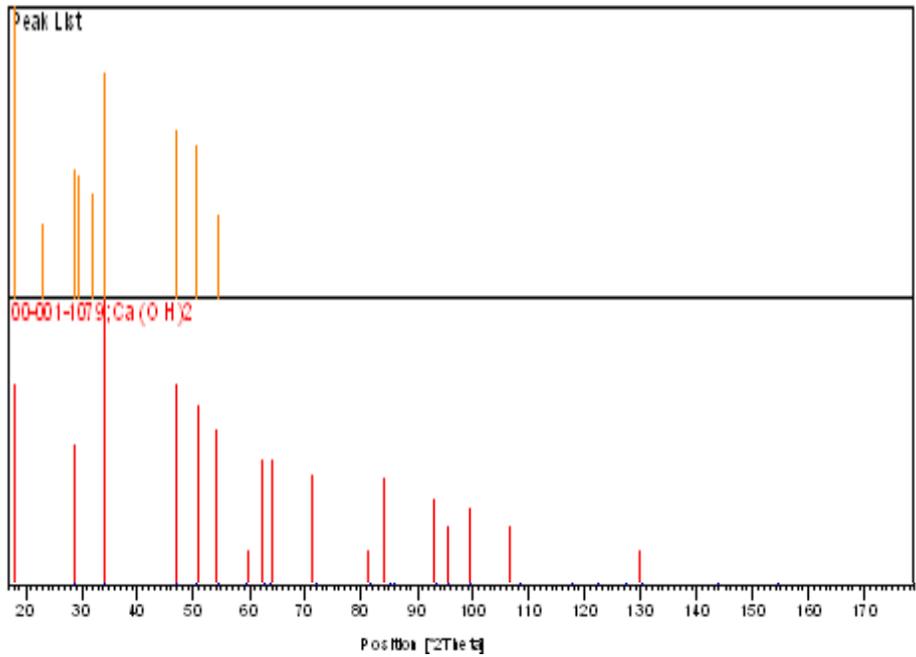


Fig. 3. Derived peak list and peak list of matching compounds for OPC specimens after one year of exposure

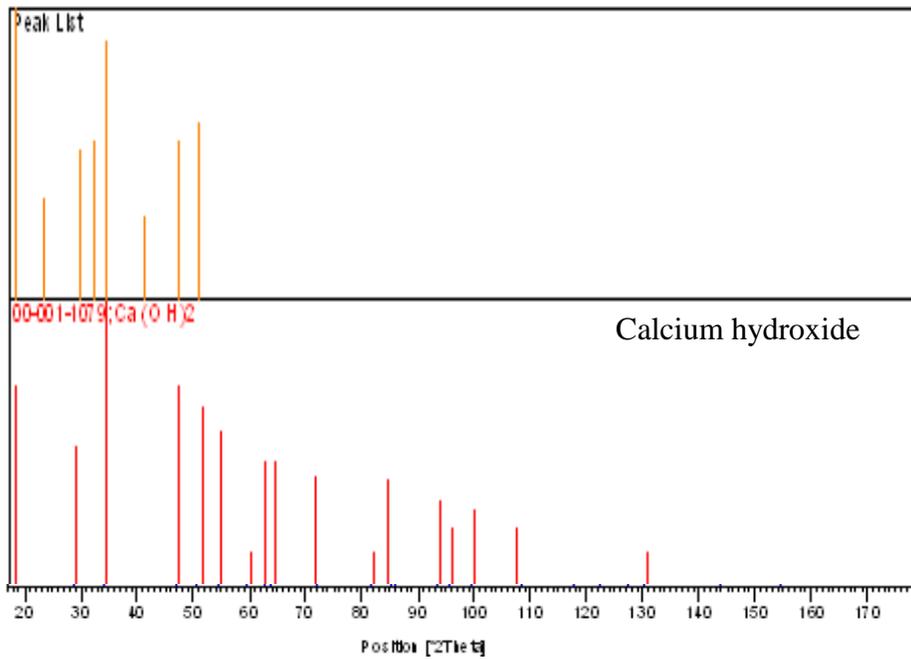


Fig. 4. Derived peak list and peak list of matching compounds for 90%OPC / 10% microsilica specimens after one year of exposure

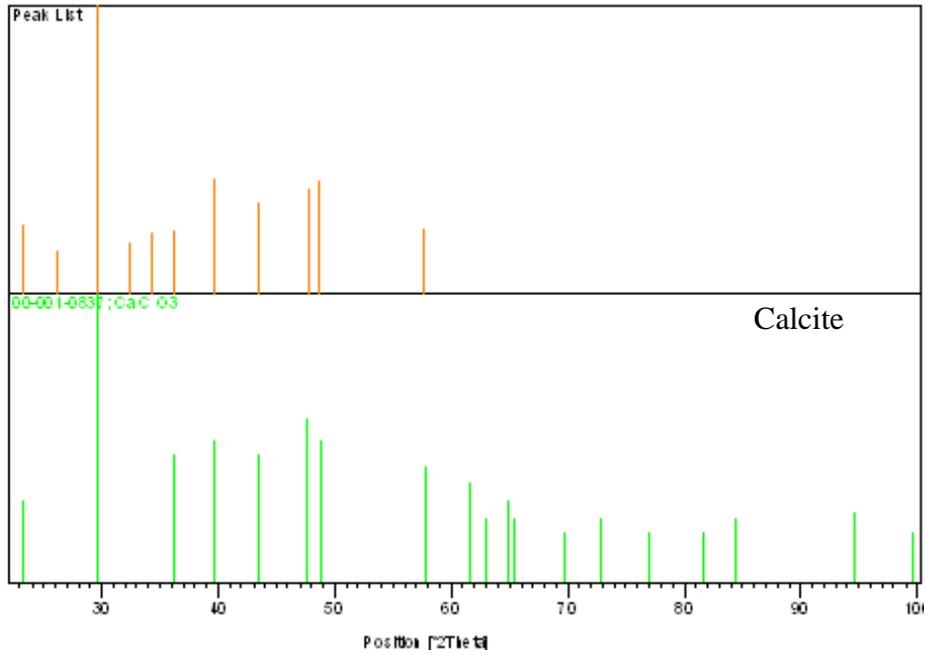


Fig. 5. Derived peak list and peak list of matching compounds for surface material from OPC specimens after one year of exposure

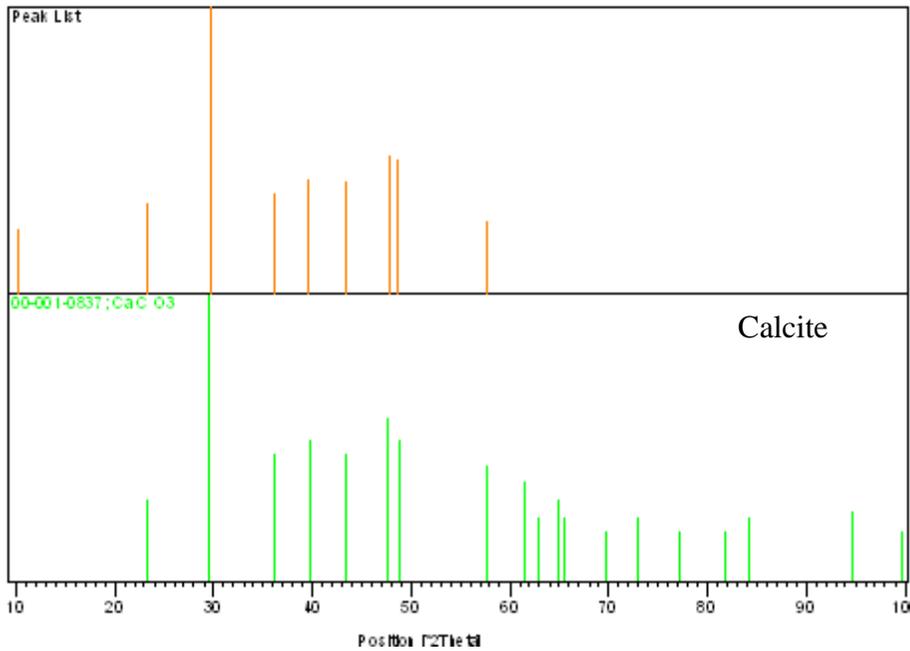


Fig. 6. Derived peak list and peak list of matching compounds for surface material from 90%OPC / 10% microsilica specimens after one year of exposure

DISCUSSION

Figures 1 and 2 illustrate the SEM images of the cut profile of OPC specimens and specimens with a 10% replacement of OPC by microsilica respectively along with their associated element maps, after 1 year of exposure. Element mapping after 1 year detects a 25-30 μm thick layer of deposits that contains calcium, carbon, phosphorus mainly in the upper half and lower quantities of sodium in the OPC specimens. A very similar layer is observed in the microsilica-containing specimens although its depth is about half the size. It is possible that in both cases this layer consists of calcium phosphates precipitating on the surface of the specimens, which is a common occurrence when de-icers contain phosphorus-based corrosion inhibitors, and recrystallised sodium acetate along with calcium carbonate [Jang, Iwasaki, & Weiblen 1995]. This may be occurring, as leaching of calcium hydroxide, encouraged by the presence of Na^+ in the solution, leads to the formation what may be a calcium phosphate compound. Such a deposit could obstruct the interaction between the specimens and their surrounding solutions, acting therefore, as a protective barrier against ion ingress [Jang, Iwasaki, & Weiblen 1995]. Alternatively, if deposited in cracks, it could enlarge their size, making the cement paste more susceptible to ingress of aggressive agents. The fact that microsilica-containing specimens demonstrate a deposit layer of smaller thickness could be another indication that the compounds therein are the ones mentioned above, since the inclusion of silica fume leads to higher consumption of calcium hydroxide and therefore its lower availability for leaching and for the formation of calcium-containing compounds on the surface.

As shown in Figures 3 and 4, X-Ray diffraction does not detect the phosphates in question or any calcium carbonate, either in OPC specimens or in microsilica-containing specimens. It is possible that both these compounds would be missed by this test due to their low quantity with respect to the ground specimens taken from the prisms. Surprisingly, these phosphates do not seem to be detected in the results of the XRD scans on material taken from the surface of both OPC and microsilica-containing specimens in Figures 5 and 6 respectively, which casts some doubt on whether the observed features are, in fact, precipitated calcium phosphates. Instead these scans detect only the presence of calcite. However, the phosphorus observed in the SEM images is a result of the inhibitor contained in the commercial sodium acetate product used in this study. The direct effects of sodium acetate however, seem to be limited to the presence of Sodium in the surface layers of the specimens, which are quite likely, deposits. It is possible that sodium, as mentioned above, encourages the leaching of calcium hydroxide. Thus, the only effect of sodium acetate on cement paste could be this accelerated leaching which is largely alleviated in the microsilica-containing prisms.

CONCLUSIONS

Sodium acetate seems to be able to melt ice at lower temperatures than NaCl and has performed satisfactorily where it has been used. Despite some concerns raised about its possible impact on the natural environment practical experience has shown no noticeable effects. This study has shown that there do not seem to be significant effects on the concrete paste which can be directly attributed to contact with the sodium acetate solution, after one year of testing. It appears, therefore, that this somewhat overlooked de-icer could be a choice worth of further research and consideration for inclusion in de-icing operations.

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