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A Reply to a Discussion by John Bensted of the Paper "CHEMICAL EFFECTS ON CEMENT MORTAR OF CALCIUM MAGNESIUM ACETATE AS A DEICING AGENT"*

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I am most thankful to Dr J. Bensted for his own experience of acetate agents and their effects on cement mortar and concrete, and for his observations of how magnesium acetate and CMA change at contact with hardened cement mortar, which I find most helpful.

I am also thankful for Dr Bensted's hint that I should be wary of mixing CMA with sodium chloride in order to reduce the cost of the deicing agent.

In his Discussion, Dr Bensted assumes that CMA, according to my paper, contains a double salt with the ions Ca^{2+}, $CH_3CO_2^-$, and OH^-, and in addition a lot of water. However, in the comments to FIG. 4 this double salt is assumed to be formed *as a result of* chemical reactions between *hardened cement paste* and *calcium acetate* solution. Thus, the double salt is not assumed to constitute a component of the CMA.

Still, it seems to me that there is a point in Dr Bensted's remark. The CMA was changed from the molar ratio Ca/Mg equal to 1.26 to the lower ratio 0.91 just because this probably would reduce the rate of attack of the calcium acetate component on the hardened mortar.

The flexural strength after storage in concentrated CMA always presented a large deviation, but for mortar prisms with the w/c ratio 0.45 the strength seemed to remain greater if the CMA of type 1.26 had been changed to type 0.91 (compared with the strength after storing in water).

Surprisingly enough, the conditions became quite different when the concentration of the CMA solution had been reduced from about 38 to 6.5 gram per 100 gram water. Now the strength of the mortars decreased, irrespective of their w/c ratios.

The table in **Conclusions** (Paragraph 2) shows that, after storage for 9 months of mortar prisms in the solution, the magnesium concentration of the dilute CMA solution decreased from 0.245 to 0.177 mol per liter, and that the calcium concentration at the same time increased from 0.223 to 0.274 mol per liter. The alterations correspond to changing part of the magnesium acetate in the CMA for calcium acetate.

In a similar way, Dr Bensted reports that after storage of mortar blocks in magnesium acetate solution, the blocks were covered with an efflorescence, the main component of which was calcium acetate (and not magnesium acetate).

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*CCR 25(3), 617 (1995)

The different solubility products of magnesium hydroxide and calcium hydroxide account for the two observations above. Calcium hydroxide gives to pure water a pH value of about 12.5. If the water contains a magnesium salt, for instance magnesium acetate, magnesium hydroxide will form as soon as the pH value of the solution exceeds about 9:

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

As a result, the magnesium acetate solution loses magnesium, which precipitates as magnesium hydroxide. The hardened cement paste loses calcium hydroxide, which makes the solution contain more and more calcium acetate.

It seems as though this calcium acetate in the solution can react further with the residual calcium hydroxide phase, thus causing an expansion of the mortar, which may be fairly strong (FIG. 1). Unfortunately, I have not found any evidence in the literature that confirms that such a calcium hydroxy acetate hydrate phase does exist, or gives information on its composition.

Some additional facts may contribute to the decreased strength after storage of mortar prisms in dilute CMA solution:

1. FIG. 3 shows an increased expansion, especially of mortar prisms with the w/c ratio 0.45.
2. FIG. 7 shows that both types of mortar prisms gain in mass during the first six months of storing.
3. TABLE 1 (next page), from (1), shows that water and the two sodium chloride solutions rapidly assume a pH level about 12 after contact with the calcium hydroxide in the hardened

TABLE 1

pH Value of Liquids During the First Six Months of Storage of Mortar Prisms at 20°C

Liquids:
1. Water
2. Sodium chloride solution - 3 gram sodium chloride per 97 gram water
3. Sodium chloride solution - saturated
4. CMA solution - 6.5 gram CMA per 100 gram water
5. CMA solution - 38.35 gram CMA per 100 gram water

Before the immersion of the mortar prisms, the liquids No 1. - 3. had such a low buffer capacity that reading of their pH values was estimated to be meaningless.

Though Liquid 4. has almost the same pH value as Liquid 5, its viscosity in all likelihood is less, and its ability to penetrate the mortar probably is correspondingly greater.

Liquid No	1.	2.	3.	4.	5.
State of storage					
Before immersion	pH value not read			9.43	9.16
1 month	12.09	12.23	11.94	9.22	9.23
2 months	12.13	12.31	12.07	8.89	9.23
3 months	11.89	12.09	11.83	9.27	9.07
4 months	12.14	12.37	12.08	9.19	9.21
5 months	12.03	12.30	12.05	8.84	9.04

cement paste. On the other hand, the two CMA solutions kept a pH level about 9. Because the calcium hydroxide phase in the hardened cement paste loses its stability in a solution with a pH value less than 12, this means that the calcium hydroxide must be consumed, owing either to precipitation of magnesium hydroxide, or to some reaction with calcium acetate in the solution.

One interesting point is Dr Bensted's statement that CMA is suspected to turn deleterious to concrete in the presence of sodium chloride. There seems to be a temptation to test this combination because its price is lower than that of pure CMA.

Reference

1. O. Peterson, "The Chemical Effects on Cement Mortar of Solutions (two different concentrations) of Calcium Magnesium Acetate and Sodium Chloride", Report TVBM-3049, Lund, Sweden (1992).