SUSCEPTIBILITY OF CONCRETE ADMIXED WITH NON-CHLORIDE ACCELERATORS TO ASR.

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The present study investigated the effect of four non-chloride accelerators, namely, calcium formate, calcium nitrate, sodium nitrite and sodium benzoate on the engineering properties of concrete. The investigation disclosed that, these materials have a drastic adverse effect on the concrete properties, particularly, at long-term ages. This has been attributed to the formation of ettringite or ettringite-analogous expansive reaction products in case of the presence of formates and to alkali-silica reactions in case of nitrates, nitrites and benzoates.

INTRODUCTION

One of the limitations to the wide use of chloride-based accelerating admixtures, particularly calcium chloride, in reinforced concrete is that, they could promote corrosion of the reinforcement, unless suitable precautions are taken. Hence, there are continuing attempts to find alternatives to chloride-based accelerators, equally effective and economical but without their limitations. A number of organic and inorganic compounds including: triethanolamine, formates, nitrates, benzoates, thiosulfates, carbonates, nitrites and chromates have been suggested. Although these materials have been used in concrete industry for many years, not much is known about their long-term effectiveness in concrete.

In a previous investigation (1), calcium formate, calcium nitrate, sodium benzoate and sodium nitrite in concrete proved to behave as efficient corrosion inhibiting admixtures.

Hoping that the presence of these materials would not adversely affect the concrete engineering properties, the present study investigated their effect upon the compressive strength of the concrete after short and long-term curing ages as well as the bond strength between the concrete and the embedded reinforcement.

EXPERIMENTAL

The ingredients of the concrete mix used in the present investigation were ordinary Portland cement, sand and gravel. The maximum size of the coarse aggregate was 10 mm. This size has been found relevant for use with the different sizes of moulds utilized. The mix proportions were 1:2:4, by weight, for cement : sand : gravel. The water/cement ratio was 0.6 by weight. Tap water was used for concrete mixing. The concrete samples containing admixtures were prepared in the same way and the required amount of admixture was dissolved in the mixing water before adding it to the dry concrete mix. The admixture was always expressed as a percentage of the cement by weight.

For carrying out the compressive strength measurements, concrete cubes 10 x 10 x 10 cm were prepared. The cubes were cured for 24 hrs, demoulded and continuously cured till the time of testing at 7,28,90 and 365 days. A set of 3 cubes was used for each compressive strength determination.

For carrying out the bond strength measurements, the concrete mix was cast into standard 10 x 20 cm cylindrical moulds in which steel rods were centered. The concrete samples were demoulded 24 hrs after casting and then cured in the humidity chamber up to 6 months. The bond strength was then determined by carrying out the pull-out tests for the steel embedded in the concrete cylinders and recording the respective loads at which initial and then ultimate slips occur. A set of 3 tests was carried out for each measurement.

For following the variations that could have resulted in the concrete hydration products due to admixture effect, as compared to a control (admixture-free) concrete, x-ray analysis has been performed on concrete samples after relevant curing.

RESULTS AND DISCUSSION

Until recently, most reseach pertaining to the use of non-chloride accelerators in concrete was concerned with reinforcement corrosion resistance, setting time and strength development in concrete particularly at short-term ages up to 28 days.

The present study investigated the effect of admixing concrete with 2% from each calcium formate, calcium nitrate, sodium benzoate and sodium nitrite in comparison with a control sample upon the compressive strength of concrete after short and long-term curing ages as well as the bond strength between concrete and the embedded reinforcement.

Compressive Strength

The compressive strength values obtained for concrete admixed with 2% from each calcium formate, calcium nitrate, sodium benzoate and sodium nitrite compared to control sample as a function of curing time are given in Fig.1. It can be seen that the compressive strength for the admixture-free concrete increases with the increase of the curing time.

Figure 1 shows that 2% calcium formate and 2% calcium nitrate have a significant effect on the short-term compressive strength of the concrete where they increase the compressive strength at 7 days by 57.1 and 51.9%, respectively, over the value obtained for the control concrete. Then, the compressive strength progressively increases with the increase of curing time up to 6 months where it reaches its maximum values. But, at the curing time of one year the compressive strength decreases by 20.6 and 23.5% relative to the values obtained at 6 months for the concrete containing 2% calcium formate and 2% calcium nitrate, respectively.

Although the values obtained at one year curing time for the concrete incorporating 2% calcium formate and 2% calcium nitrate still exceed those obtained for the control concrete by 8.6 and 9.4%, respectively, one cannot rely on that slight apparent increase over the control concrete strength values since this adverse effect could extend by the coarse of time beyond one year and reduce the concrete strength below that of the control concrete.

In case of admixing concrete with 2% sodium benzoate and 2% sodium nitrite, their effect is worse. The short-term compressive strength has slightly exceeded the values obtained for the control concrete while the long-term compressive strength obtained at one year has seriously reduced below the values of the control concrete. Treadaway, et al (2) found that both sodium nitrite and sodium benzoate tremendously reduce the strength of the concrete after 28 days curing.

Bond Strength

The effect of the used admixtures on the bond strength between the concrete and the embedded reinforcement after 6 months and one year curing has been investigated. The results of such measurements are presented in Fig.2. It is evident that, the adverse effects of the used non-chloride accelerators on the engineering propertics of concrete extended to include the bond strength between the concrete and its embedded reinforcement. Figure 2 shows that, the ultimate bond strength gained after one year decreases by 14.0, 14.6, 19.6 and 14.8 relative to the bond strength gained after 6 months for the concrete incorporating 2% from each calcium formate, calcium nitrate, sodium benzoate and sodium nitrite, respectively.

X-ray diffraction analysis of concrete after long-term curing in presence of non-chloride accelerators

It deemed of interest to identify and compare the phases formed in concrete incorporating the used non-chloride accelerators at curing ages of 6 months and one year which could be responsible for the adverse effects on the concrete properties after long-term curing ages. Hence, x-ray diffraction analysis has been performed on parts of concrete crushed dureng the compressive strength measurements after 6 months and one year curing.

Indeed, the x-ray diffraction patterns obtained for concrete admixed with 2% calciun formate did not disclose significant changes that could be relied upon to interpret the adverse effects on the concrete engineering properties.

However, Ramachandran (3) reported that, in presence of calcium formate, the complex $C_3A. 3Ca(HCO_2)_2. 30H_2O$, analogous to ettringite is formed at ordinary temperatures. Also, Gebler (4) found that the chemical composition of the cement, in particular its SO_3 content, has a major influence on the compressive strength development of concretes containing calcium formate. Such concretes showed accelerated compressive strengths when low sulfate cements were used.

Bearing the above-mentioned in mind, the reduction in the mechanical properties of concrete admixed with 2% calcium formate at long-term curing ages may be attributed to the formation of ettringite or ettringite-analogous expansive reaction products that, by the coarse of time, induce internal pressures sufficient to disrupt the concrete, thus, reducing its strength. Also, it is to be mentioned that, most of the cement plants are currently producing Portland cements with high SO_3 contents due to more economical methods of cement production. This would affect the long-term mechanical properties of concrete. Consequently, the suitability of calcium formate to be used as a non-chloride accelerator in reinforced concrete is suspicious.

The x-ray diffraction analysis of the concrete incorporating 2% calcium nitrate and 2% sodium nitrite (Figs. 3 and 4) revealed an interesting feature. In both cases, the quartz content-as indicated by the corresponding peak intensities-has decreased appreciably after one year curing age relative to its content after 6 months age. Such behavior emphasizes that, an alkali-silica reaction-that usually occurs when reactive siliceous materials and cement with high alkali content are used in concrete-has occurred in both cases. According to Powers, et al , (5) and Lea (6), reactive siliceous materials in presence of high concentration of alkali (above 0.6 %) give reaction products which are predominantly gels formed of alkali silicates containing certain amount of lime. Such gels have large expansive properties upon imbibition of water. It has been reported (7), also, that manifestations due to alkali-aggregate reactions in concrete may appear only after months or even years.

Thus, it may be concluded that, both calçium nitrate and sodium nitrite initiate alkali-silica reactions in concrete leading eventualy to reductions in concrete strength that start to appear at ages beyond 6 months. These reactions may be assisted in case of calcium nitrate by the acidic nature of the No^{-}_{3} ion, as a salt of a strong acid. Also, in case of sodium nitrite the alkali-silica reactions may be accentuated due to the No^{-}_{2} ion as well as the presence of Na^{+} that increases the alkali content of the medium.

To ascertain the foregoing conclusion, the alkali content (i.e. Na_2O + K_2O) of concrete admixed with 2% calcium nitrate and 2% sodium nitrite has been determined. It has been found that, the alkali content amounts to 1.3% and 2.0% in the concrete incorporating 2% calcium nitrate and 2% sodium nitrite, respectively. As far as the authors are aware of, such long-term effect of calcium nitrate and sodium nitrite on concrete has never been reported in the literature.

X-ray diffraction analysis of concrete incorporating 2% sodium benzoate after curing ages of 6 months and one year indicated that, sodium benzoate promoted the alkali-silica reaction in concrete but to a lesser extent than in case of calcium nitrate or sodium nitrite.

It is to be mentioned that, the drastic adverse effects, particularly, of sodium nitrite and sodium benzoate on the engineering properties of concrete after long-term service make their usage as concrete admixtures questionable.

CONCLUSIONS

1. The adverse long-term effects of the investigated non-chloride accelerators, namely, calcium formate, calcium nitrate, sodium benzoate and sodium nitrite, on the mechanical properties of concrete make their suitability to be used as admixtures in concrete questionable inspite of their effectiveness as corrosion inhibitors.

2. The effects of the non-chloride accelerators used in the present investigation and many others on the properties of hardened concrete at long-term ages seem to indicate a fruitful field for future work.

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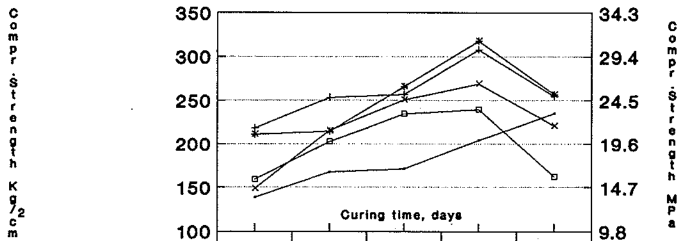
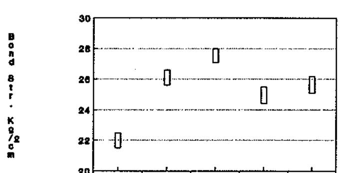


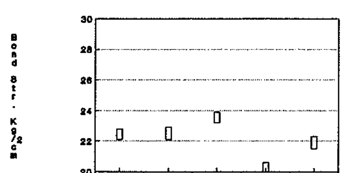
	7	28	90	180	365
0% Admixture	138.8	167.3	171.4	204	235
2% Ca-Formate	218.1	253.2	257	307.8	255.1
2% Ca-Nitrate	210.8	214.7	266	317.7	257.1
2% Na-Benzoate	159	202.5	234.4	240	162.4
2% Na-Nitrate	148.7	215.7	251	269	221

Fig. (1): Compressive strength of concrete admixed with 2 % from each calcium formate, calcium nitrate, sodium benzoate and sodium nitrite compared to admixture-free concrete as a function of curing time .



	A	B	C	D	E
Ultimate Str.	22.5	26.6	28	25.5	26.2
Initial Str.	21.5	25.6	27.1	24.4	25.1

6 Months Curing



	A	B	C	D	E
Ultimate Str.	22.8	22.9	23.9	20.6	22.3
Initial Str.	22.1	22.1	23.2	20	21.6

1 Year Curing

Fig. (2): Bond strength for reinforcing steel in concrete incorporating 2 % from each calcium formate (B), calcium nitrate (C), sodium benzoate (D), and sodium nitrite (E) compared to admixture-free concrete (A) cured for 6 months & 1 year, Kg/cm2.

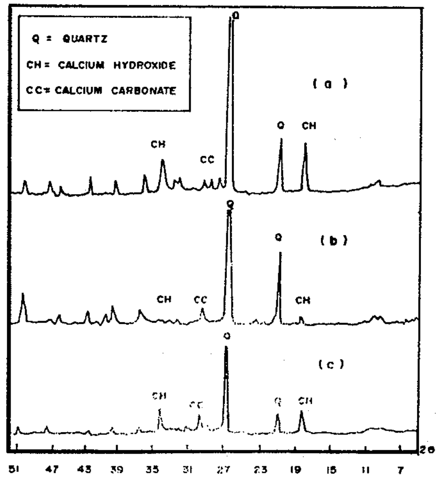


FIG. (3) : XRD PATTERNS OF CONCRETE ADMIXED WITH 2 % CALCIUM NITRATE CURED FOR 6 MONTHS (b) AND ONE YEAR (C) COMPARED TO THE PATTERN OBTAINED AFTER CURING FOR 7 DAYS (a)

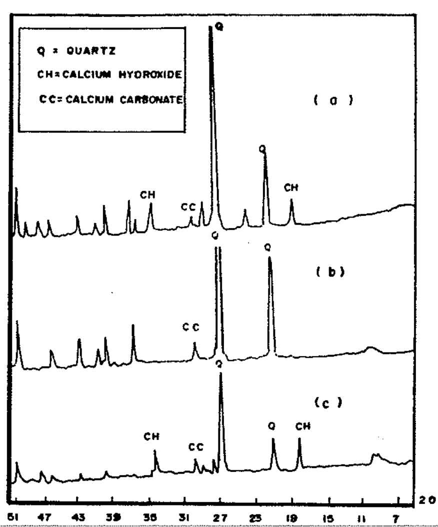


FIG. (4) : XRD PATTERNS OF CONCRETE ADMIXED WITH 2 % SODIUM NITRITE CURED FOR 6 MONTHS (b) AND ONE YEAR (c) COMPARED TO THE PATTERN OBTAINED AFTER CURING FOR 7 DAYS (a)