

Quick method to determine free and bound chlorides in concrete

MARIO COLLEPARDI

Department of Science of Materials and Earth, University of Ancona, Ancona (Italy)

Abstract

A colorimetric method based on spraying fluoresceine and then a silver nitrate solution has been developed to determine the presence of free chloride. The method can be used to determine the presence of free chloride from mix ingredients, provided that the amount of Cl^- is higher than 0.0012% by weight of concrete. The method can be used to determine the time taken for free chloride from mix ingredients to be transformed into bound chloride: this time is shorter than 1 month, provided that free Cl^- from mix ingredients is not higher than that accepted for reinforced concrete structures by ENV 206 pre-norm.

The method can also be used to determine the concrete thickness penetrated by Cl^- diffusion in concrete specimens or structures permanently exposed to a chloride aqueous solution such as marine structures fully immersed in sea water.

The method must be modified with a preliminary re-alkalinization treatment to determine the concrete thickness penetrated by Cl^- in structures discontinuously exposed to chloride aqueous phase and/or air carbonation, such as marine structures in the splash zone or highway concrete structures exposed to deicing salts.

Key-words: Free chloride, Bound chloride, Chloride diffusion, Chloride penetration, Carbonation.

1 Introduction

Chloride salts can promote corrosion of steel reinforcement in concrete structures. Chlorides may come from two sources:

- a) as contaminant of mix ingredients in the fresh concrete (water, cement, aggregates) or as accelerating chemical admixture up to about 1% by weight of cement;
- b) as deicing salts or sea water from the environment in contact with the hardened concrete in service.

Independently of the above mentioned sources, chlorides may be found in different states:

- 1) bound chloride, chemically combined with *C-A-H* in form, for instance, of $C_3A \cdot CaCl_2 \cdot 10H_2O$;
- 2) bound chloride, adsorbed on *C-S-H*;
- 3) free chloride ions within the pore aqueous solution.

It is generally assumed that only free chloride ions can promote the corrosion process of steel reinforcement (1). On the other hand, free chloride can be gradually transformed into bound chloride. If so, after a certain period of time, chloride should no more be available to promote the corrosion of steel reinforcement. In other words, the transformation of free chloride into bound chloride should reduce or even eliminate the corrosion caused by the presence of chloride, provided that the source of chloride from the environment is blocked. Such a transformation should make harmless the defined amount of chloride in the concrete ingredients, whereas should play a negligible role for the chloride from an unlimited environmental source.

2 A colorimetric method for free and bound chlorides

To distinguish the free chloride from the bound one, a colorimetric method has been developed by Colleparidi et al in 1970 (2, 3) which has been subsequently used as a standard method in Italy to determine the chloride penetration into concrete structures (4). This method is based on the spraying of fluoresceine (1 g/l in a 70% of ethyl alcohol in water) and then of silver nitrate aqueous solution (0.1 M $AgNO_3$) on the concrete fractured surface area. In the absence of chloride, or in the presence of bound chloride only, the concrete surface is permanently pink-coloured; on the other hand, in the presence of free chloride, $AgCl$ is produced which, when exposed to natural light, quickly becomes dark-coloured because of a photochemical process.

In the present work, this quick colorimetric method has been assessed for the following purposes:

- a) to determine the minimum amount of free chloride content which can be detected by this method;
- b) to determine how much time is taken for the free chloride (from concrete ingredients) to be transformed into the harmless bound form;
- c) to determine the Cl^- diffusion in concrete specimens permanently exposed to chloride aqueous solution;
- d) to determine the concrete depth penetrated by Cl^- ions in concrete structures discontinuous exposed to chloride aqueous solution and/or to carbon dioxide in the air.

3 Experimental

The work includes two different sections. The first one is devoted to examine the chloride content (originated by concrete ingredients through predetermined additions of $NaCl$); this section covers the above mentioned *a* and *b* purposes. The second section of the present

work is devoted to study the chloride penetration from the environment into concrete specimens or structures according to the above mentioned *c* and *d* purposes.

3.1 Chloride from concrete ingredients

Five concrete mixes have been manufactured, the main difference being the various amount of sodium chloride dissolved in mixing water. The percentage of chloride was from 0.01 to 0.60% by weight of cement, corresponding to 0.0012% and 0.0073% by weight of concrete (Table 1). In the concrete mix No. 1 with the lowest chloride content, sodium chloride was not added to mixing water and the 0.01 percentage is due to the chloride present in the cement only. Some specimens have been manufactured from each concrete mix. After a curing time of 1, 3, 7, 14 and 28 days the specimens were splitted and the fractured surface areas were treated with fluoresceine and $AgNO_3$.

Table 1. Mix proportions and chloride content of concrete specimens

| Mix No. | 1 | 2 | 3 | 4 | 5 |
|----------------------------------|--------|-------|-------|-------|-------|
| Cement (kg/m ³) | 298 | 308 | 304 | 302 | 298 |
| Water (kg/m ³) | 149 | 154 | 152 | 151 | 149 |
| Sand (kg/m ³) | 798 | 795 | 804 | 806 | 802 |
| Gravel (kg/m ³) | 1205 | 1210 | 1190 | 1190 | 1198 |
| Cl ⁻ (% by w. cem.) | 0.01 | 0.10 | 0.20 | 0.40 | 0.60 |
| Cl ⁻ (% by w. concr.) | 0.0012 | 0.013 | 0.025 | 0.050 | 0.073 |

The results obtained in the present work demonstrate that even a very small amount of free chloride, such as 0.01% by weight of cement or 0.0012% by weight of concrete, can be detected by the colorimetric method, provided that the test is carried out at very early ages (1 day). At later ages (for instance 3 days) the free chloride is transformed into bound chloride and the pink-coloured surface turns into the dark one (Fig. 1).

The same colour change from pink to dark (and the corresponding change from free to bound chloride) occurs even in the specimens with higher chloride content. However, the change of colour requires longer times by increasing the chloride content. For instance, the specimen with 0.6% chloride by weight of cement (corresponding to 0.073% by weight of concrete) needs 28 days to change the colour from pink to dark. Table 2 illustrates the change from free to bound chloride as a function of curing time and chloride content. The higher the chloride content as "contaminant" of the mix ingredients, the longer is the time required to transform the free dangerous chloride into the bound harmless one.

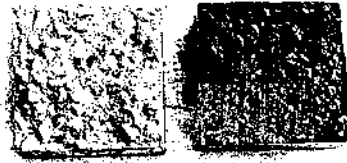


Fig. 1. Pink-coloured (left) and dark-coloured surfaces of the concrete specimen with 0.01% chloride (by weight of cement) from concrete ingredients at 1 day and 3 days respectively.

These results indicate that the amount of total chloride from concrete ingredients accepted for reinforced or prestressed structures by the European ENV 206 pre-norm, (0.4% or 0.2% respectively by weight of cement) is really harmless from the corrosion point of view: in less than 1 month the original free Cl⁻ ions are transformed into the bound chloride form which is not more available to promote the corrosion of reinforcing bars.

Table 2. The effect of curing time on the change from free to bound chloride from concrete ingredients.

| Curing time (days) | Chloride content (% by w. of cem.): | | | | |
|--------------------|-------------------------------------|-------|-------|-------|-------|
| | 0.01 | 0.10 | 0.20 | 0.40 | 0.60 |
| 1 | Free | Free | Free | Free | Free |
| 3 | Bound | Free | Free | Free | Free |
| 7 | Bound | Bound | Free | Free | Free |
| 14 | Bound | Bound | Bound | Free | Free |
| 28 | Bound | Bound | Bound | Bound | Bound |

3.2 Chloride from the environment

Chloride ions can penetrate the concrete cover in two different environmental conditions:

- i) Cl⁻ ions can diffuse through the pore aqueous solution in concrete structures permanently exposed to a chloride aqueous phase: this occurs, for instance, in concrete structures fully immersed in sea water;
- ii) Cl⁻ ions can penetrate concrete by a diffusion mechanism and/or by capillary suction of salt water in the pore system of the cement matrix: this occurs, for instance, in marine structures of the splash zone or in concrete slabs discontinuously exposed to deicing salts.

In condition *i*, chloride diffusion is not accompanied by CO₂ penetration since the exposure to air is permanently excluded. In condition *ii*, the carbonation of the concrete cover can occur in the absence of the aqueous phase with or without Cl⁻ ions. Since the colorimetric method has been developed (2, 3) for laboratory concrete specimens permanently exposed to a chloride aqueous phase in the absence of CO₂, - condition *i* - the extension of this method to real concrete structures exposed to the penetration of both Cl⁻ and CO₂ (4) - condition *ii* - should be checked.

Figure 2 shows three concrete cube specimens permanently exposed to a chloride aqueous solution (10% NaCl) with a full, partial or negligible chloride diffusion: the dark-coloured area corresponds to a chloride-free concrete (Cl⁻ less than 0.0012% by weight of concrete) and the pink-coloured area corresponds to a chloride-penetrated concrete.

Figure 3 shows chloride-free concrete specimens, all exposed to carbonation in the absence of any chloride source. After splitting a cube specimen, the fractured surface area has been treated with phenolphthaleine: the grey-coloured area shows the concrete portion which has been penetrated by CO₂, whereas the red-coloured area corresponds to a lime-rich concrete with a pH higher than 13 (on the left hand of Fig 3).

An other cube specimen (on the middle of Fig. 3) has been treated with fluoresceine and AgNO₃ on the fractured surface area: although no free chloride was available and no chloride penetration has occurred, a pink-coloured concrete depth appears as thick as the grey-coloured depth in the previous specimen treated with phenolphthaleine. This means that, even in the absence of chloride, the dark-coloured concrete turns into the pink-coloured one just for the pH change caused by carbonation only. Therefore, in order to be sure that the change from the dark colour into the pink one is related selectively and exclusively with chloride penetration, a preliminary alkaline treatment (for instance with a 10% NaOH aqueous solution) is required for the concrete surface before the subsequent treatment with fluoresceine and AgNO₃. The cube specimen on the right hand of Fig. 3 has been treated with 10% NaOH to re-establish a pH higher than 13 in the carbonated area, and then with fluoresceine and AgNO₃; after this double treatment, the fractured surface area appears completely dark in agreement with no chloride penetration.

The above results indicate that the colorimetric method to detect the chloride penetration depth in real concrete structures exposed to both Cl⁻ and CO₂ can be advantageously adopted, provided that the pH of the surface is artificially re-established at the original level (> 13) by a preliminary alkaline treatment.



Fig. 2. Concrete specimens exposed to Cl^- diffusion from a NaCl aqueous solution: the dark-coloured area corresponds to the chloride-free concrete portion.



Fig. 3. Concrete specimens exposed to CO_2 penetration in the absence of chloride; on the left hand: the specimen treated with phenolphthaleine; on the middle: the specimen treated with fluoresceine and AgNO_3 ; on the right hand: the specimen treated with fluoresceine and AgNO_3 after a preliminary treatment with NaOH .

4 Conclusions

Even a very small amount of chloride, which is present as contaminant of the mix ingredients (0.01% by weight of cement corresponding to 0.00125% by weight of concrete), can be detected in the concrete specimen by the colorimetric test based on fluoresceine and AgNO_3 , provided that the test is carried out within 1 day of curing. After this period of time the transformation from free chloride to the bound one does not allow to determine the presence of this amount of chloride. Higher percentages of free Cl^- up to 0.6% by weight of cement (corresponding to 0.073% by weight of concrete), are completely converted into the bound form within 28 days. This means that chloride ions, initially present as contaminant of the mix ingredients or as chemical admixtures, are not available to corrosion within about 1 month, provided that the amount of chloride is lower than a certain amount of Cl^- such as 0.6% by weight of cement. This value is higher than the accepted chloride content in concrete ingredients (0.4% and 0.2% for reinforced and prestressed structures respectively) according to the european ENV 206 pre-norm.

The same colorimetric method may be used to determine the thickness of concrete penetrated by Cl^- diffusion when concrete specimens or structures are permanently exposed to a chloride aqueous phase such as for marine structures fully immersed in sea water.

The method must be modified, with a re-alkalization process (10% NaOH aqueous solution) before the treatment of the concrete surface with fluoresceine and AgNO_3 , for concrete structures exposed discontinuously to Cl^- salts and/or carbonation such as marine structures in the splash zone or highway concrete slabs exposed to deicing salts.

References

1. Arya, C., Buenfield, N. R. and Newman, J. B., "Assessment of simple methods of determining the free chloride ion content of cement paste", *Cem. Concr. Res.* 17, (1987) 907-918.
2. Collepardi, M., Marcialis, A., and Turriziani, R., "The kinetics of chloride ions penetration in concrete (in Italian), *Il Cemento*, 67, (1970)157-64.
3. Collepardi, M., Marcialis, A., and Turriziani, R., "Penetration of chloride ions in cement pastes and in concretes", *J. Am. Cer. Soc.*, 55, (1972) 534-535.
4. UNI 7928, Italian norm to determine the penetration of chloride ions in concrete structures (1978).