CHLORIDES IN CONCRETE

CTI TECHNICAL NOTE C2

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INTRODUCTION

When steel reinforcement is encased in sound dense concrete, the entire surface of the steel is covered by a stable protective oxide film that forms in the alkaline environment created by the hydration of the cement in the concrete. Under these circumstances no corrosion of the reinforcement can occur.

However, if the protective oxide film is locally destroyed, for example by the ingress of chloride ions, areas of different potential can be set up on the surface. Steel encased in concrete with its protective film intact will have a more noble potential than steel without the protection of the alkaline environment.

This difference in potential can result in electrochemical corrosion cells forming between areas on the reinforcement where the protective film has been destroyed and the remainder of the surface where the film is still intact. Such cells create minute electric currents which flow through the reinforcement in one direction and return through the concrete by electrolytic conduction.

The areas where the electrons leaves the reinforcement to enter the concrete are called *anodes* and they corrode, whereas the areas where the current re-enters the reinforcement do not corrode and are called *cathodes*. Corrosion takes place at the anode with metal ions going into solution (refer Eqn. 1)

$$Fe \rightarrow Fe^{++} + 2e^- \qquad (1)$$
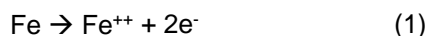
No corrosion occurs at the cathode, the cathode simply provides the mechanism for the removal of electrons left in the reinforcement by the corrosion process (refer Eqn. 2).

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2)$$
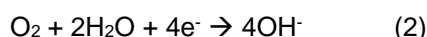
The concrete must be wet enough to provide an electrolytic path for the transport of ions and therefore the corrosion of reinforcement in dry concrete is minimal even if areas of different potential exist.

There are two ways that the protective oxide film that forms on steel reinforcement in sound concrete might be destroyed. These are the reduction of the pH of the concrete by carbonation, and the ingress of chloride ions.

UNITS FOR EXPRESSING CHLORIDE CONTENT OF CONCRETE

PART PER MILLION (ON CONCRETE)

The fundamental unit for chloride content of concrete as determined by analysis is a concentration by weight of the sample analysed (ie. concrete). This is usually expressed as a percentage of the weight of the concrete or as "parts per million" (ppm) by weight of concrete, hereafter shown as ppm_{conc}. 1,000 ppm_{conc} is equal to 0.1% chlorides by weight of concrete.

KILOGRAM PER CUBIC METRE OF CONCRETE

The units for chloride content of concrete used in AS 1379 and AS 3600 are weight of chlorides in kilograms per cubic metre of concrete, expressed as kg/m^3.

To convert ppm_{conc} to these units, the density of the concrete needs to be known or assumed. If a concrete density of 2,400 kg/m^3 is assumed, then 1,000 ppm_{conc} equals 2.4 kg/m^3.

CHLORIDES AS A PERCENTAGE BY WEIGHT OF CEMENT

Not all of the chloride ions in concrete exist in a free state. Some chlorides can become bound in the cement (principally in the C3A phase), especially if present in the original mix. As a result, higher cement contents often impart a higher tolerance to total chlorides. When considering the durability of concrete or the likelihood of chloride-induced corrosion of the reinforcing steel, the most relevant way of expressing chloride concentrations is as a proportion of the cement.

Therefore for durability investigations or specifications, the chloride content is most commonly expressed as a concentration of chlorides in the binder, and is usually expressed as a percentage by weight of the cement, or "%bwoc".

However to convert analytical results to %bwoc, the cement content must be known. If the mix design is known, the theoretical cement content can be calculated. Otherwise the cement content may be determined by analysis (also as weight percent on the concrete).

For example, if the cement content is 350 kg/m^3 and the density of the concrete is 2,400 kg/m^3, the cement content will be:

$$\frac{350}{2,400} \times 100 = 14.6\%$$

To convert an analytical result for the chloride content of ppm$_{conc}$ to %bwoc, divide it by the cement content as a percentage, and divide again by 100.

For example if the analytical result for the chloride content is 1000 ppm$_{conc}$, and if the cement content is 14.6%:

$$1,000\text{ppm}_{conc} \rightarrow \frac{1,000}{14.6 \times 100} = 0.69\% \text{ bwoc}$$

THRESHOLD CONCENTRATIONS

Thresholds for chlorides in <u>new</u> concrete normally refer to total or acid soluble chlorides.

AS 1379 and AS 3600 specify a limit of 0.8 kg/m^3. This is approximately equal to 330 ppm$_{conc}$ (assuming a density of 2,400 kg/m^3).

If the cement content is then assumed to be of 350 kg/m^3, a chloride content of 0.8 kg/m^3 would equal 0.23 %bwoc.

AS 2758.1-1985 gave upper chloride limits of 0.2 and 0.4% bwoc for reinforced concrete in severe and moderate exposure environments respectively, and 0.1% bwoc for pre-stressed structures. These equate as follows:-

%bwoc	kg/m^3 (assuming 350kg cement)	ppm$_{conc}$ (assuming 14.6% cement content)
0.1	0.35	146
0.2	0.7	292
0.4	1.40	584

The 1998 revision of AS 2758.1 does not contain these thresholds. In Europe, BS 8110: Part 1-1997 and BS EN 206-1:2000 both have a limit of 0.4% bwoc for all reinforced concrete.

These thresholds are also used by those assessing the condition of existing concrete structures, and the usual interpretation is that when these are exceeded, the reinforcing steel is in danger of succumbing to chloride-induced corrosion.

However whether or not corrosion actually commences above the chloride threshold, and the rate at which corrosion progresses, will both depend on other factors, including the moisture content of the concrete and its resistivity (which are also related to each other) and the degree of alkalinity of the concrete.

If the pH (a measure of alkalinity) remains above 13, and if the concrete has a relatively high resistivity (> ~15 kΩcm), then chloride induced corrosion is not likely to be a problem even at twice the threshold level.

On the other hand, moderately carbonated concrete (ie. medium alkalinity) in a moist environment will create ideal conditions for chloride-induced corrosion to commence at or above the threshold levels.

METHODS FOR DETERMINING CHLORIDE CONTENT OF CONCRETE

CHLORIDE CONTENT OF HARDENED CONCRETE

The chloride content of hardened concrete can be determined by chemical analysis, using AS 1012.20-1992, ASTM C 1152-97 or BS 1881 Part 124-1988. The latter involves a more simple extraction procedure.

All three of these standards are for the determination of total or "acid soluble" chlorides. Essentially the powder sample is digested in nitric acid to dissolve the cement matrix and liberate all the chlorides present. The extract is then analysed for chloride ion content using a Volhard titration, a chloride ion selective electrode or similar technique.

In addition to the free chlorides present in the pore water or capillaries of the concrete, any chlorides added to the mix and "bound" in the cement phase will also be detected by these methods.

For water-soluble or "free" chloride determination, the concrete sample is extracted by refluxing with boiling water. This is not however a common procedure except in the US.

All of the above analytical methods first require the concrete to be sampled. Powder samples extracted by hammer drill are suitable, as are crushed samples from core sections.

The sampling procedure should avoid wet methods which might wash out chlorides from the concrete and lead to an ambiguous or lower result. If cores are taken for chloride analysis using wet coring, the diameter should be at least 40 mm.

CHLORIDE CONTENT OF FRESH CONCRETE

The chloride content of fresh concrete can be determined from its constituent ingredients. The chloride content of the cement (if not provided by the manufacturer) can be determined using the same methods as for hardened concrete.

For the aggregates and make-up water, the chloride content can be determined using standard analytical procedures. Additives should have a known (and low) chloride content; if testing is required suitable methods may be found in the literature or by consulting the suppliers.

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