



Chloride Content of Fresh Concrete

Introduction

Corrosion of steel reinforcement is a significant concrete durability problem in New Zealand. It is caused by the depth or quality of cover concrete being insufficient to prevent moisture and air penetrating the concrete surface and migrating to the reinforcement, and is exacerbated when the concrete contains chloride ions.

In addition to increasing the risk of reinforcement corrosion after construction, chlorides can affect the setting behaviour of fresh concrete and its subsequent strength

development. They can also increase the risk of efflorescence. It is therefore important to minimise the amount of chlorides in both fresh and hardened concrete.

Chlorides may originate from the concrete materials themselves when the concrete is mixed, or from exposure to seawater, sea-spray or chloride-based de-icing salts once the structure is in service. This Information Bulletin describes the procedures used to measure and control the amount of chloride ion added to fresh concrete when it is mixed.

Control of Chloride Content

Where Do The Chlorides in Fresh Concrete Come From?

Although chloride ions are present in most concrete constituents, the most significant sources are calcium chloride accelerators (which should not be used in reinforced concrete), aggregates and the mix water.

New Zealand rocks do not contain significant amounts of chloride within their constituent minerals, but aggregates may be contaminated with sea salts, especially if they are derived from a marine source or stockpiled near the coast.

The New Zealand Drinking-Water Standard (2000) specifies a maximum chloride content of 250g/m^3 of water, so the contribution from a treated drinking water supply should be minimal. Recycled wash water, however, may contain chlorides from other mix components and the water used for washing. Untreated water may contain chlorides from seawater or groundwater. To manage this, ASTM C1602-04 includes optional limits for chlorides in combined mix water of 500 ppm for prestressed concrete,

bridge decks or other designated structures, and 1,000 ppm for other reinforced concrete, although these limits may be exceeded if the amount of chloride in the concrete is less than a certain amount (see below).

Free, Bound, Acid-soluble and Water Soluble Chlorides

Chlorides exist in concrete in three forms:

- Chloride ions dissolved in the pore water (“free chlorides”);
- Chloride ions chemically bound to the hydrated cement paste (“bound chlorides”);
- Chloride ions chemically bound within the minerals that make up the aggregate.

Free and bound chlorides are sourced from soluble salts present in the concrete materials or on the surface of aggregates. Although they may be contaminated with surface deposits of salt, New Zealand aggregates generally consist of rock types that do not contain significant amounts of chloride-

bearing minerals, so the free chlorides plus the bound chlorides closely approximate the total chloride content of New Zealand concrete.

“Water soluble” chlorides are those that are dissolved by extraction in water. They approximate the free chlorides, depending on the analytical method used. “Acid soluble” chlorides are those that are dissolved by extraction in nitric acid. They include free and bound chlorides but do not include chlorides in the minerals that make up the rock. Water soluble chloride content is not a constant percentage of acid-soluble chloride but varies with the amount of chloride present, the mix constituents and the analytical test methods used.

Free chlorides initiate corrosion by depassivating the steel, and may also increase the subsequent corrosion rate. Bound chlorides do not directly take part in corrosion, but may eventually dissolve to become free chlorides. It is difficult to predict how much of the chloride in fresh concrete will remain free and how much will be bound once the concrete hardens, so it is prudent to include both when controlling the amount of chloride present in fresh concrete. Bound chlorides are included in the “acid soluble” chlorides specified by NZS 3101 (see page 3), but only some bound chlorides are included in

the “water soluble” chlorides specified by other documents such as ACI 222 and ACI 318.

Limits on Chloride Content

To reduce the risk of reinforcement corrosion being caused by chloride ion contamination in fresh concrete, the New Zealand Concrete Structures Standard (NZS 3101) specifies that the acid-soluble chloride content of concrete based on measurements of chloride content sourced from aggregate mixing water and admixtures shall not be greater than the values shown in **Table 1**. If chloride contents calculated for a particular mix exceed the relevant limit, the materials must be changed or the mix modified to reduce the chloride content¹.

The chloride content of fresh concrete is calculated by adding together the amounts of acid soluble chloride contributed by each constituent by the formula shown on page 3.

Suppliers of manufactured constituents such as cement, admixtures and SCM's and other materials should be able to provide information on the chloride content of their products. The following sections describe how to obtain the chloride ion content of aggregate and water.

Table 1: Maximum Values of Chloride Ion Content in Concrete as Placed

Type of Member	Maximum Acid Soluble Chloride Ion Content (kg/m ³ of Concrete)
Prestressed concrete	0.50
Reinforced concrete exposed to moisture or chloride in service	0.80
Reinforced concrete that will be dry or protected from moisture in service	1.6

¹ Commentary to ACI 318 suggests that acid-soluble chlorides be used for an initial evaluation of a mix, and if the chloride content thus obtained exceeds the permitted limits then it may be necessary to test the concrete to find out whether it meets requirements for water-soluble chloride ion content. ACI 222 describes the use of a test for measuring free chlorides in concrete that does not meet requirements for water-soluble chlorides. This Information Bulletin is restricted to NZS 3101 requirements and does not include evaluation of water-soluble or free chlorides.

$$Cl_{\text{total}} = \frac{(NF \times MF) + (NC \times MC) + (NA \times MA) + (NCem \times MCem) + (NSCM \times MSCM) + (NW \times MW)}{100}$$

where Cl_{total} = acid-soluble chloride content of the concrete, expressed as kg/m^3 chloride

NF = chloride ion content of the fine aggregates as a percentage by mass of dry aggregate

MF = fine aggregate content in kg/m^3

NC = chloride ion content of the coarse aggregate as a percentage by mass of dry aggregate

MC = coarse aggregate content in kg/m^3

NA = chloride ion content of the admixture(s) as a percentage by mass of the admixture

MA = admixture content(s) in kg/m^3

Ncem = chloride ion content of the cement as a percentage by mass of cement

Mcem = cement content in kg/m^3

NSCM = chloride ion content of supplementary cementitious material (SCM) as a percentage by mass of SCM

MSCM = SCM content in kg/m^3

NW = chloride ion content of water as a percentage by mass of water

MW = water content in kg/m^3

Measuring the Chloride Content of Aggregate

NZS 3101:1995 requires that when testing to determine the acid soluble chloride ion content, test procedures shall be in accordance with ASTM C1152. BS 1881: Part 124:1988, AS 1012.20, or x-ray fluorescence spectroscopy (XRF) are acceptable alternative procedures.

ASTM C1152, BS 1881: Part 124:1988 and AS 1012.20 involve preparing acid extracts from the aggregate and analysing the extracts by wet chemical techniques. XRF is more convenient than wet chemical techniques because the aggregate itself can be analysed, and therefore is the recommended method. Where the chlorides are predominantly in the form of sea salt

contamination, as in most New Zealand aggregates, results from XRF analyses of total chlorine generally do not differ significantly from wet chemical analyses of chloride content.

An IANZ-accredited chemistry laboratory with experience in chemical analysis of rocks and minerals should perform the analysis. A list of these laboratories is available on the IANZ website's Directory page. The laboratory should be instructed to analyse for total chlorine by XRF, or for chloride ion by ASTM C1152, BS 1881: Part 124:1988 or AS 1012.20 (it may be helpful to provide the laboratory with one of these standard test methods because although the analysts may

not know these particular standards they may be familiar with the procedures involved).

Testing laboratories offering XRF analysis will sub-sample and crush the sample in

preparation for its analysis. For analysis by wet chemical methods, the sample may need to be prepared by another laboratory, and the testing laboratory will advise on how to arrange this if necessary.

Measuring the Chloride Content of Water

When Does it Need to be Measured?

Analyses of water from New Zealand municipal water supplies prior to 1995 can be accessed from the JASPER database held by the Institute for Environmental Science and Research (ESR). Drinking water composition does not vary greatly over time, so old analytical data is generally acceptable unless there has been a major change in the supply since the most recent analysis. Specific chemical analysis of town supplies used for concrete mix water should not be necessary. The limit for NZ drinking water (250g/m^3) may be used instead of measuring the chloride content of a specific supply if analytical results are unavailable

Non-potable water supplies, including recycled wash water, do need to be analysed. Recycled wash water may contain chlorides from other mix constituents, and other sources may be contaminated with soil or marine salts.

It is strongly recommended that recycled or other non-potable water supplies be sampled and analysed over several weeks to obtain a range of typical operating chloride contents. The maximum value obtained should be used in calculations of concrete chloride content.

How to Measure It

The chloride contents measured will be determined by the way the water is sampled, particularly for recycled water. It is important that the sample taken for analysis represents the water as it is delivered to the concrete mixer. For recycled water this means including suspended solids. All sampling equipment and containers must be clean, and should be rinsed with the water before collecting the sample. The chemistry laboratory performing the analysis will be able to advise how much

water should be sampled, and how it should be stored and delivered to the laboratory.

For potable water, analyses should be performed according to an internationally recognised Standard for drinking water, such as those published by the American Public Health Association (APHA) or similar organisations. Analytical techniques commonly used include ion chromatography (IC), and titration. The water should be analysed by a commercial chemistry laboratory that is IANZ accredited for analysing drinking water for chloride ion. A list of these laboratories is available on the IANZ website's Directory page. The laboratory must be instructed to analyse the water sample for chloride ions.

For water containing suspended solids (e.g. recycled wash water), the total chlorides in the solids must be included in the analysis. The easiest way to do this is to analyse the sample for total chlorine by XRF. An IANZ-accredited chemistry laboratory with experience in chemical analysis of rocks and minerals should perform this analysis. A list of these laboratories is available on the IANZ website's Directory page.

Further Reading

More detailed information on the effects and control of chloride ions in concrete can be found in ACI 201, ACI 222R and ACI 318.



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