CASE No. 3: Plain Concrete + Admixtures containing 0.5% Cl⁻

Now, assume hypothetically that both HRWRA and AEA in CASE No. 2 contain a chloride ion content of 0.5 percent by mass of the admixture. The amounts of chlorides contributed by the two admixtures now become,

HRWRA: $\dfrac{975 \text{ mL}}{100 \text{ kg}} \times 386 \text{ kg/m}^3 \times \dfrac{1.28 \text{ g/mL}}{1000} \times 0.5\% \text{ Cl}^- = 0.0241 \text{ kg Cl}^-/\text{m}^3$

AEA: $\dfrac{130 \text{ mL}}{100 \text{ kg}} \times 386 \text{ kg/m}^3 \times \dfrac{1.28 \text{ g/mL}}{1000} \times 0.5\% \text{ Cl}^- = 0.003 \text{ kg Cl}^-/\text{m}^3$

CASE No. 4: Plain Concrete + an Admixture containing 22% Cl⁻

For comparison, assume that the concrete was treated with 2080 mL/100 kg of an admixture with a chloride ion content of 22 percent by mass. Assuming the same density for the admixture, the amount of chlorides contributed by the chloride-bearing admixture is,

$\dfrac{2080 \text{ mL}}{100 \text{ kg}} \times 386 \text{ kg/m}^3 \times \dfrac{1.28 \text{ g/mL}}{1000} \times 22\% \text{ Cl}^- = 2.261 \text{ kg Cl}^-/\text{m}^3$

The total chloride ion contents for the four cases discussed above are summarized in Table 3A.

Table 3A. Effects of Admixtures on Calculated Chloride Contents of Concrete Calculated Total Chloride Content (kg/m³)

Concrete Ingredient	CASE No. 1	CASE No. 2	CASE No. 3	CASE No. 4
Plain Concrete	0.300	0.300	0.300	0.300
AEA	_	0.0003	0.003	_
HRWRA	_	0.024	0.024	_
Chloride Admixture	_	_	_	2.261
Total	**0.300**	**0.303**	**0.327**	**2.561**
CHLORIDE ION CONTENT OF CONCRETE (% of cementitious materials)	0.078	0.079	0.085	0.664

Comparing the data for CASE No.1 and CASE No.2 shown in Table 3 (Table 3A), it can be seen that the nonchloride-bearing admixtures will increase the total chloride ion content of the concrete by ONLY 0.001 percent by mass of cementitious materials. The data also show that, even if their chloride ion content was increased to 0.5 percent by mass, the nonchloride-bearing admixtures would increase the total chloride ion content of the concrete by ONLY 0.006 percent by mass of cementitious materials. These increases are very negligible and within the ACI CODE-318 limits for reinforced concrete exposed to chlorides in service.

By contrast, the calculations show that 32 fl oz/cwt (2080 mL/100 kg) of typical chloride-bearing admixture will increase the total chloride content by 0.588 percent by mass of cementitious materials. In accordance with the ACI CODE-318 requirements, such a concrete mixture would not be suitable for use in reinforced concrete structures that will be exposed to chlorides in service.

It should be noted, however, that in accordance with the ACI CODE-318 requirements, samples of the hardened concrete may be tested for water-soluble chlorides between 28 and 42 days to determine if the limits would be met. This is due to the fact that a portion of the chlorides present in the concrete at the time of placement would be bound up in the hardened matrix during the hydration process. These chlorides, as mentioned earlier, will typically not contribute to the corrosion process.

Conclusions

The following conclusions can be drawn from the information presented in this publication:

1) It is practically impossible to develop an admixture that is completely free of chlorides.

2) Claims that the chloride limit for nonchloride-bearing admixtures should be no more than 0.05 percent by mass of admixture (500 parts per million) are unfounded.

3) The use of a nonchloride-bearing admixture with a chloride ion content of no more than 0.5 percent by mass of admixture (5000 parts per million) will only result in a marginal increase in the total chloride ion content of the concrete.

4) Chloride-bearing admixtures can contribute significantly to the total chloride ion content of concrete and should be used as appropriate.

Suggested Specification for Admixtures

Consistent with current ACI CODE-318 provisions for chemical admixtures, the following specification language is recommended:

1. Calcium chloride or admixtures containing intentionally-added chlorides shall not be used in nonprestressed and prestressed concretes.

2. Chloride ion content calculations shall be performed in accordance with ACI CODE-318 if required.

References

1. Millar, W. and Nichols, C.F., "Improvements in Means of Accelerating the Setting and Hardening of Cements." Patent 2886, London, England, March 4, 1885.

2. CONCRETE ADMIXTURES HANDBOOK-Properties, Science, and Technology, Edited by Ramachandran, V.S., Noyes Publication, Park Ridge, New Jersey, 1984, 626 pp.

3. ACI CODE-318-19 Building Code Requirements for Structural Concrete and Commentary, American Concrete Institute, Farmington Hills, Michigan, 623 pp.

4. ACI SPEC-301-20 Specifications for Concrete Construction, American Concrete Institute, Farmington Hills, Michigan, 69 pp.

5. Monfore, G.E. and Verbeck, G.J., "Corrosion of Prestressed Wire in Concrete", Journal of the American Institute, Vol. 32, No. 4, Nov. 1960, pp. 491-515.

6. Spellman, D.L. and Stratfull, R.F., "Chlorides and Bridge Deck Deterioration", State of California, Division of Highways – Materials and Research Department, Research Report No. M&R635116-4, Nov. 1969, 29 pp.

7. ACI PRC-201.2-16 Guide to Durable Concrete, American Concrete Institute, Farmington Hills, Michigan, 82 pp.

8. ACI PRC-222-19 - Guide to Protection of Metals in Concrete Against Corrosion, American Concrete Institute, Farmington Hills, Michigan, 60 pp.

9. ASTM C1152/C1152M-20 Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, ASTM International, West Conshohocken, Pennsylvania, 4 pp.

10. ASTM C1152/C1152M-20 Standard Test Method for Water-Soluble Chloride in Mortar and Concrete, ASTM International, West Conshohocken, Pennsylvania, 3 pp.

11. Berman, H.A., "Determination of Chloride in Hardened Portland Cement Paste, Mortar, and Concrete", Report No. FHWA-RD-72-1, Federal Highway Administration, Sept. 1972, 22 pp.

12. ASTM C1524-20 Standard Test Method for Water-Extractable Chloride in Aggregate (Soxhlet Method), ASTM International, West Conshohocken, Pennsylvania, 5 pp.

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Concrete Technology in Focus

Chlorides and Admixtures

Introduction

Chlorides are derived from chlorine, a nonmetal which, like oxygen, is one of the basic elements that exists in nature. Chlorides can be found in most materials in at least very small quantities that may not be detectable, or in large quantities such as in sodium and calcium chloride. Sodium chloride is commonly known as table salt, and until recently, calcium chloride was widely used to accelerate the set of portland cement.

The accelerating effect of calcium chloride on the set of portland cement has been known since 1885[1]. This effect, combined with the beneficial effect of calcium chloride on early strength development, resulted in its use either exclusively or as a major ingredient in accelerating admixtures for concrete[2]. Admixtures that contain intentionally-added calcium chloride or other compounds of chloride are typically referred to as chloride-bearing. Likewise, admixtures that do not contain intentionally-added chlorides are referred to as nonchloride-bearing.

Because chlorides exist naturally in most materials, they are likely to be present in trace amounts even in so-called nonchloride admixtures. The chlorides present in these nonchloride admixtures are often referred to as background chlorides. The amount of chloride ions present in an admixture from chloride compounds in its constituent materials is typically expressed as a percentage of the mass of the admixture or in parts per million (ppm). Chloride-bearing admixtures may contain approximately 22 percent (220,000 parts per million) of chloride ions by mass compared to less than 0.3 percent (3,000 parts per million) for nonchloride-bearing admixtures.

Because of the potential adverse effect of chlorides on corrosion of reinforcement, ACI CODE-318, Building Code Requirements for Structural Concrete and Commentary[3], prohibits the use of calcium chloride or admixtures containing intentionally-added chlorides in nonprestressed or prestressed concrete. However, ACI SPEC-301, Specifications for Concrete Construction[4], only prohibits the use of calcium chloride in concrete members assigned to Exposure Classes S2 or S3. Both ACI CODE-318 and ACI SPEC-301 provide limits for the maximum water-soluble chloride ion content in concrete. However, neither ACI CODE-318 nor ACI SPEC-301 limit the chloride ion content of nonchloride-bearing admixtures. Some admixture manufacturers in the past have claimed, without basis, that nonchloride-bearing admixtures should contain no more than 0.05 percent of chloride ions by mass. This claim is totally unfounded and erroneous, and engineers need to be aware of the issues and guidelines regarding the chloride ion content of concrete mixtures. As shown later in this publication, nonchloride-bearing admixtures with a chloride ion content of 0.5 percent by mass will contribute only a very small fraction of the total chloride ion content of most concrete mixtures.

Current ACI Limits on Chloride Ion Content

Despite the beneficial effects of chlorides on the time of set and early strength development of portland cement concrete, numerous studies have shown that when present in sufficient quantities, chloride ions will promote the corrosion of steel in concrete[5,6]. This has led to restrictions on the amount of chloride ions allowed in concrete prior to service exposure. Currently, three ACI technical committees have established allowable chloride ion limits for concrete; namely, ACI 201-Committee Durability of Concrete[7], ACI 222-Committee Corrosion of Metals in Concrete[8] and ACI CODE-318-Committee Structural Concrete Building Code[3]. A summary of the limits recommended in ACI PRC-222 and ACI CODE-318 are shown in Table 1.

Table 1. ACI Recommended Chloride Ion Limits for Concrete Prior to Service Exposure.

	ACI PRC-222-19 Chloride Limit (% by mass of cementitious material)		ACI CODE-318-19 Water-soluble	
	Acid-soluble	**Water-soluble**		**Chloride limit*** (% by mass of cement)
Category	**ASTM C1152/C1152M**	**ASTM C1218/C1218M**	**Type of Member**	
Prestressed Concrete	0.08	0.06	Prestressed Concrete	0.06
Reinforced Concrete in wet conditions	0.20	0.08	Nonprestressed concrete that will be exposed to moisture and an external source of chlorides from deicing chemicals, salt, brackish water, seawater, or spray from these sources	0.15
Reinforced Concrete in dry conditions	0.30	0.15	Nonprestressed concrete that will be dry or protected from moisture	1.00
			Nonprestressed concrete that will be exposed to moisture but not to an external source of chlorides	0.30

*Based on calculating total chloride ion content of the concrete mixture on the basis of measured total chloride ion content from concrete materials and concrete mixture proportions or on water-soluble chloride determined in accordance with ASTM C1218 at age between 28 to 42 days.

As can be seen from Table 1, while ACI PRC-222 recommends limits based on acid-soluble and water-soluble chloride tests, ACI CODE-318 recommends limits based only on the water-soluble chloride test. Because of its status as the Building Code Requirements for Structural Concrete, design engineers should specify the limits recommended in ACI CODE-318.

Testing for Chlorides in Concrete

The amount of chloride ions present in concrete or in its constituents is typically determined analytically by using either the acid-soluble or water-soluble chloride test methods. The acid-soluble test method measures that chloride which is soluble in nitric acid and therefore includes chloride ions that are bound within the hardened matrix, including the aggregates.

The water-soluble test method on the other hand only measures that chloride which is extractable in water under specific conditions. Compared to the acid-soluble test, this method is less reliable because of the effect that factors such as extraction time, temperature, sample size, and concrete age have on the results obtained.

Of the two, the acid-soluble test method is more commonly used because of its reliability even though the measured chloride ion content includes chlorides that may not pose a problem with regard to corrosion.

Research studies performed at the Federal Highway Administration[11] (FHWA) and elsewhere indicated that, on average, the water-soluble chloride ion content of concrete is about 50 to 75 percent of the acid-soluble chloride ion content of the same concrete. However, because of the inherent variability in the water-soluble chloride test method, this range is not absolute.

Chlorides in concrete are usually bound within the hardened matrix, including the aggregates, in addition to being present in the pore solution. It is generally accepted by corrosion experts that only the chloride ions readily available in the pore solution pose a problem with regard to the corrosion of steel in concrete. The ASTM C1152/C1152M[9] and ASTM C1218/C1218M[10] chloride test methods involve the use of pulverized material and as such do not distinguish between bound and unbound chlorides in aggregates. In 2002, ASTM International approved ASTM C1524, "Standard Test Method for Water-Extractable Chloride in Aggregate (Soxhlet Method)[12]," primarily for use with aggregates that contain high levels of chloride that may not pose a problem with respect to corrosion.

Calculating Chloride Ion Contents in Concrete using ACI CODE-318

In Section 26.4.2.2 (e) of ACI CODE-318-19, it is noted that:

"Compliance with the specified chloride ion content limits shall be demonstrated by (1) or (2).

(1) Calculating the total chloride ion content of the concrete mixture on the basis of measured materials and mixture proportions.

(2) Determining water-soluble chloride ion content of hardened concrete in accordance with ASTM C1218 at age between 28 and 42 days."

Example Calculation from Concrete Ingredients (in.-lb Units)

Calculating the chloride ion content of concrete using chloride ion contents obtained for the individual ingredients is a relatively simple procedure as outlined below.

1. Determine the proportion (mass, dosage, etc.) of each of the concrete ingredients, Wi.

2. Obtain the chloride ion content of each ingredient, [Cl]i (as a percent by mass of the ingredient).

3. To determine the amount of chloride ions contributed by each ingredient (except admixtures), perform the following calculation:
   Chloride ions contributed by ingredient = Wi x [Cl]i

4. To determine the amount of chloride ions contributed by an admixture, use Eq. 1.

(Eq. 1)
Chlorides contributed by the admixture (lb/yd³) =

$$\frac{\text{Admixture Dosage fl oz}}{100 \text{ lb}} \times \frac{\text{Cementitious Materials Content}}{\text{lb/yd}^3} \times \frac{\text{Density of Admixture lb/gal}}{128 \text{ fl oz/gal}} \times \frac{\text{Chloride Ion Content of Admixture}}{\% \text{ Cl}^-}$$

5. Add the chloride ion contributed by each ingredient and divide the total by the mass of cementitious materials in the mixture (expressed as a percentage).

For illustration purposes, consider the following four cases for concrete containing 650 lb/yd³ of of cement and a water-cementitious materials ratio of 0.40.

CASE No. 1: Plain Concrete (no Admixtures)

The amount of chlorides contributed by the basic concrete ingredients is as shown in Table 2.

Table 2. Sample Chloride Ion Content Calculation for Plain Concrete Based on Concrete Ingredients

Concrete Ingredient	Amount (lb/yd³)	Chloride Ion* Content (%)	Calculation	Chloride Ions Contributed (lb/yd³)
Cement	650	0.0022	650 x 0.0022%	**= 0.014**
Fine Aggregate	1230	0.0113	1230 x 0.0113%	**= 0.139**
Coarse Aggregate	1800	0.0160	1800 x 0.016%	**= 0.288**
Water	260	250 ppm	260 x 250 x 10⁻⁶	**= 0.065**
			TOTAL	**= .506**
Therefore,		CHLORIDE ION CONTENT OF CONCRETE (% of cementitious materials)	$\frac{0.506 \times 100}{650}$	**0.078%**

* Nominal chloride ion content in ingredient by mass

CASE No. 2: Plain Concrete + Admixtures containing 0.05% Cl⁻

Assume that the concrete mixture in CASE No. 1 was treated with 15 fl oz/cwt of a high-range water-reducing admixture (HRWRA) and 2 fl oz/cwt of an air-entraining admixture (AEA), both with a chloride ion content of 0.05 percent by mass of admixture. The amounts of chlorides contributed by the two admixtures assuming that a gallon of admixture weighs 10.7 lb are:

HRWRA: $\frac{15 \text{ fl oz}}{100 \text{ lb}} \times 650 \text{ lb/yd}^3 \times \frac{10.7 \text{ lb/gal}}{128 \text{ fl oz/gal}} \times 0.05\% \text{ Cl}^- = 0.004 \text{ lb Cl}^-/\text{yd}^3$

AEA: $\frac{2 \text{ fl oz}}{100 \text{ lb}} \times 650 \text{ lb/yd}^3 \times \frac{10.7 \text{ lb/gal}}{128 \text{ fl oz/gal}} \times 0.05\% \text{ Cl}^- = 0.0005 \text{ lb Cl}^-/\text{yd}^3$

CASE No. 2: Plain Concrete + Admixtures containing 0.5% Cl⁻

Now, assume hypothetically that both HRWRA and AEA in CASE No. 2 contain a chloride ion content of 0.5 percent by mass of the admixture. The amounts of chlorides contributed by the two admixtures now become,

HRWRA: $\frac{15 \text{ fl oz}}{100 \text{ lb}} \times 650 \text{ lb/yd}^3 \times \frac{10.7 \text{ lb/gal}}{128 \text{ fl oz/gal}} \times 0.50\% \text{ Cl}^- = 0.041 \text{ lb Cl}^-/\text{yd}^3$

AEA: $\frac{2 \text{ fl oz}}{100 \text{ lb}} \times 650 \text{ lb/yd}^3 \times \frac{10.7 \text{ lb/gal}}{128 \text{ fl oz/gal}} \times 0.50\% \text{ Cl}^- = 0.005 \text{ lb Cl}^-/\text{yd}^3$

CASE No. 4: Plain Concrete + an Admixture containing 22% Cl⁻

For comparison, assume that the concrete was treated with 32 fl oz/cwt of an admixture with a chloride ion content of 22 percent by mass. Assuming the same density for the admixture, the amount of chlorides contributed by the chloride-bearing admixture is:

$\frac{32 \text{ fl oz}}{100 \text{ lb}} \times 650 \text{ lb/yd}^3 \times \frac{10.7 \text{ lb/gal}}{128 \text{ fl oz/gal}} \times 22\% \text{ Cl}^- = 3.825 \text{ lb Cl}^-/\text{yd}^3$

The total chloride ion contents for the four cases discussed above are summarized in Table 3.

Table 3. Effects of Admixtures on Calculated Chloride Contents of Concrete Calculated Total Chloride Content (lb/yd³)

Concrete Ingredient	CASE No. 1	CASE No. 2	CASE No. 3	CASE No. 4
Plain Concrete	0.506	0.506	0.506	0.506
AEA	–	0.0005	0.005	–
HRWRA	–	0.004	0.041	–
Chloride Admixture	–	–	–	3.825
Total	**0.506**	**0.511**	**0.552**	**4.331**
CHLORIDE ION CONTENT OF CONCRETE (% of cementitious materials)	0.078	0.079	0.085	0.666

Example Calculation from Concrete Ingredients (Metric Units)

Calculating the chloride ion content of concrete using chloride ion contents obtained for the individual ingredients is a relatively simple procedure as outline below.

1. Determine the proportion (mass, dosage, etc.) for each of the concrete ingredients, Wi.

2. Obtain the chloride ion content of each ingredient, [Cl]i (as a percent by mass of the ingredient).

3. To determine the amount of chloride ions contributed by each ingredient (except admixtures), perform the following calculation:
   Chloride ions contributed by ingredient = Wi x [Cl]i

4. To determine the amount of chloride ions contributed by an admixture, use Eq. 1A.

(Eq. 1)
Chlorides contributed by the admixture (lb/yd³) =

$$\frac{\text{Admixture Dosage mL/100 kg}}{} \times \frac{\text{Cementitious Materials Content}}{\text{kg/m}^3} \times \frac{\text{Density of Admixture (g/mL)/1000}}{} \times \frac{\text{Chloride Ion Content of Admixture}}{\% \text{ Cl}^-}$$

5. Add the chloride ion contributed by each ingredient and divide the total by the mass of cementitious materials in the mixture (expressed as a percentage).

For illustration purposes, consider the following four cases for concrete containing 386 kg/m³ of cement and a water-cementitious materials ratio of 0.40.

CASE No. 1: Plain Concrete (no Admixtures)

The amount of chlorides contributed by the basic concrete ingredients is as shown in Table 2A.

Table 2A. Sample Chloride Content Calculation for Plain Concrete Based on Concrete Ingredients

Concrete Ingredient	Amount (kg/m3)	Chloride Ion* Content (%)	Calculation	Chloride Ions Contributed (kg/m³)
Cement	386	0.0022	386 x 0.0022%	**= 0.008**
Fine Aggregate	730	0.0113	730 x 0.0113%	**= 0.082**
Coarse Aggregate	1068	0.0160	1068 x 0.016%	**= 0.171**
Water	154	250 ppm	154 x 250 x 10⁻⁶	**= 0.039**
			TOTAL	**= .300**
Therefore,		CHLORIDE ION CONTENT OF CONCRETE (% of cementitious materials)	$\frac{0.300 \times 100}{386}$	**0.078%**

* Nominal chloride ion content in ingredient by mass.

CASE No. 2: Plain Concrete + Admixtures containing 0.05% Cl⁻

Assume that the concrete mixture in CASE No. 1 was treated with 975 mL/100 kg of a high-range water-reducing admixture (HRWRA) and 130 mL/100 kg of an air-entraining admixture (AEA), both with a chloride ion content of 0.05% by mass of the admixture and density of 1.28 g/mL. The amounts of chlorides contributed by the two admixtures are:

HRWRA: $\frac{975 \text{ mL}}{100 \text{ kg}} \times 386 \text{ kg/m}^3 \times \frac{1.28 \text{ g/mL}}{1000} \times 0.05\% \text{ Cl}^- = 0.0024 \text{ kg Cl}^-/\text{m}^3$

AEA: $\frac{130 \text{ mL}}{100 \text{ kg}} \times 386 \text{ kg/m}^3 \times \frac{1.28 \text{ g/mL}}{1000} \times 0.05\% \text{ Cl}^- = 0.0003 \text{ kg Cl}^-/\text{m}^3$