Acid-Soluble and Water-Soluble Chloride – Testing Proficiency and Specification

Warren South[1], William A. Thomas[2] and Vute Sirivivatnanon[3]

[1] Director - Research & Technical Services, Cement Concrete & Aggregates Australia
[2] Chief Engineer-Concrete, Boral Construction Materials and Cement
[3]Professor of Concrete Engineering, University of Technology Sydney

Abstract: The importance of limiting the chloride ion content in concrete has always been recognised and specified in structural concrete specifications. The Australian Standard test method for acid-soluble chloride has been revised and published as AS 1012.20.1- 2015. At the same time, a newly developed water-soluble chloride test method has been published as a parallel Australian Standard AS 1012.20.2-2015. The paper reviews and reports the proficiency of the two test methods and the relationship between acid- and water-soluble chloride based on research and proficiency testing programs conducted by Cement Concrete and Aggregates Australia (CCAA). Performance limits specified in international concrete standards are reviewed and recommended to be specified in relevant Australian standards and specifications.

Keywords: Acid-soluble, water-soluble, chloride, performance limit.

1. Importance of limiting chloride ion content

Importance of limiting chloride ion content Chloride-induced corrosion of steel reinforcement has been found to be one of the most common causes of premature deterioration of reinforced and prestressed concrete structures. The more vulnerable structures are those exposed to external sources of chloride such as from marine environments or from the use of de-icing salts. Chlorides can also come from concreting materials and hence it is important that limits are placed on chlorides from these sources including cement, supplementary cementitious material (SCM), aggregates and chemical admixtures.

Chlorides can exist as surface contaminant as well as chloride-bearing minerals in the aggregates. In hardened concrete, chlorides exist as either '*bound'* or '*free'* chloride in concrete. Chlorides can be bound as reaction products between chlorides and cement hydrates such as calcium chloroaluminate (Friedels salt). It is well recognised (ACI 222R and Byfors *et al.,* 1986) that it is the free chloride that contributes to steel depassivation and subsequent corrosion. In determining the amount of chlorides in concrete, both *'water-soluble'* and *'acid-soluble (total) chloride'* test methods have been used to determine the *'free'* and *'free + bound'* chloride respectively. Bound chloride is therefore the difference between acid-soluble (total) and water-soluble chloride.

Glass and Buenfeld (2000) found that the time to corrosion initiation of embedded steel, due to chloride diffusion from the surface of concrete, to be dependent on the corrosion risk presented by bound chloride. Bound chloride may participate in corrosion initiation when the establishment of pH gradients are required to sustain passive film breakdown. This is the result of the effect on the pore solution chemistry of the pH dependent solubilities of solid phases containing bound chloride that are very similar to that of calcium hydroxide. In some circumstances, the time to corrosion initiation may be reduced by an increase in binding because of the possible corrosion risk presented by bound chloride. Hence both free and bound chlorides are equally important and must be controlled.

2. Development of water-soluble chloride testing method

In 2007, Cement Concrete & Aggregates Australia (CCAA) began the development of a water-soluble chloride testing method. Up to that time, there was very limited work carried out on the difference between water-soluble and acid-soluble chloride in aggregates. Hope *et al.* (1985) focused work on the influence of different testing techniques and sample subdivision on the resultant free water-soluble chloride. They found that subdivision of aggregate samples resulted in extraction of some chloride from the aggregate material that field experience with the aggregate used suggested that this chloride did not materially contribute to corrosion of the embedded steel. They also found that the Soxhlet (high temperature) extraction of ½ inch material was effective in recovering added chloride from the concrete samples and did not extract chloride from chloride-bearing minerals in the aggregate. They suggested that the Soxhlet extraction removed only the chloride which was mobile and able to take part in the corrosion process. In 1996, ACI Committee 222 has adopted a ‘Provisional Standard Test Method for Water-Soluble Chloride Available for Corrosion of Embedded Steel in Mortar and Concrete Using the Soxhlet Extractor’.

There have been reported instances (Gaynor,1985) where quarried stone, gravels and natural sand contained small amounts of chloride that have provided concrete with chloride levels that exceed the permissible levels of 0.2% chloride by mass of cement, the upper limit recommended in ACI 222R. Other reports (Rogers and Woda, 1977) of aggregates with an acid-soluble chloride content of more than 0.1 percent of which less than one-third is water soluble when the aggregate is pulverized for the test. Not all of that chloride will necessarily become available to the paste. Thus ACI 222R indicates that higher levels are tolerable if past performance has shown that the higher chloride content has not caused corrosion.

CCAA investigated the effectiveness of the extraction of water-soluble chloride methods, including the Soxhlet method, in terms of the type of extracting agent and degree of fractured surface of the aggregates. It was found that the use of boiling water on materials passing 850-micron sieve offered a well-balanced measure of the free chloride contents in aggregate. The findings were also confirmed valid in testing hardened concrete (Sirivivatnanon, Thomas & Waye, 2011). The methods and results of the investigation were the basis for the development of an Australian test method for water-soluble chloride.

3. Proficiency of Australian Standard testing methods

Both the accuracy and proficiency of test methods are important to their successful applications. CCAA initiated and conducted proficiency programme for the existing acid-soluble chloride test method AS 1012.20 and the draft water-soluble chloride test method in 2010 and 2011 respectively. Details and findings are described below.

3.1 AS 1012.20 Acid-soluble test method

A proficiency programme on acid-soluble chloride was conducted based on the AS 1012.20 test method. This programme focused exclusively on the analysis of chloride content and did not examine the possible variability due to sampling technique. Samples of three sands C1, C2 and C3, with a range of chloride contents were prepared by Boral Laboratory and sent to seven NATA registered laboratories around Australia.

Six laboratories submitted the results as listed below. One of these six laboratories tested replacement samples after reporting damages to the first samples. The results are summarised in Table 1.

There are inconsistencies in the reporting of test result in both the number of decimal points and significant figures. There appears also to be a limit to the accuracy of the method with some laboratories unable to test sand such as C2 and C3, with chloride content below 0.01%, to an accuracy of 0.001%. This is possibly due to the analytical method used by various laboratories ranging from Mohr’s and Volhard’s titration to potentiometry using various ion-selective electrodes.

Table 1 AS 1012.20 acid-soluble chloride test results (%)

Sand samples Lab	C1		C2		C3	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
1	0.0533	0.0517	0.0016	0.0013	0.0009	0.0008
2	0.044	0.044	<0.001	<0.001	<0.001	<0.001
3	0.038	0.043	0.004	0.009	0.003	<0.002
4	0.05	0.05	<0.01	<0.01	0.01	0.01
5	0.006	0.008	0.001	0.001	0.002	0.001
6	0.0210	0.0230	<0.005	<0.005	<0.005	<0.005
Mean	0.036		(0.0042)*		(0.0035)*	
Repeatability SD	0.0017		-		-	
Reproducibility SD	0.0179		-		-	

SD=standard deviation
( )*mean of test results using the upper limits eg. 0.001 as upper limit for <0.001.

For C1 with the mean chloride content is well in excess of 0.01%, the repeatability and reproducibility standard deviations are 0.0017 and 0.0179% respectively. The repeatability standard deviation is within the same range as 0.0015% reported in the ASTM C1152 - Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete. However, the reproducibility standard deviation of 0.0179% is significantly higher than 0.0021% reported in the ASTM C1152. For sand C2 and C3 with lower chloride contents, it is not possible to determine the precision of the method. The cause of such differences in results from various laboratories is unknown, but highlights the need for re-examination of the test procedures.

It should be noted that the AS 1012.20 Acid-soluble chloride test method is re-issued as AS 1012.20.1 in 2014 with no significant changes to the method.

3.2 Draft AS 1012.20.2 Water-soluble chloride test method

CCAA sought collaboration from the same seven laboratories to conduct proficiency tests on water-soluble chloride content in accordance with the draft water-soluble chloride determination for aggregates and hardened concrete test method. Three aggregates (CL6, CL7 & CL10) and one chloride solution were prepared by Boral Materials Technical Services and sent to all laboratories. Six laboratories submitted the results as listed in Table 2.

Four out of six laboratories reported the concentration of the standard solution fairly accurately between 33 to 38 mg/L for the solution which was prepared at 35.45 mg/L. Laboratory 1 & 2 reported higher solution concentrations and generally higher results for the three aggregates.

All laboratories are able to report results to 0.001% which is an improvement on the accuracy when conducted to AS 1012.20. The repeatability and reproducibility standard deviations for all three aggregates are similar to those reported in ASTM C1218 – Standard Test Method for Water-Soluble Chloride in Mortar and Concrete.

Table 2 Analysis of all results (%)

Sand samples	CL6		CL7		CL10		Solution*1	Notes
Lab/Sample	1	2	1	2	1	2	mg/L	
1	0.010	0.010	0.009	0.009	0.017	0.019	45	or 0.0045% solution
2	0.008	0.008	0.008	0.008	0.025	0.025	43	or 0.0012N solution
3	<0.001	<0.001	0.001	0.001	0.015	0.015	36	Potentiometric titration on -150µm
4	0.0015	-	0.0014	-	0.0147	-	38	or 0.0038% solution
5	0.0022	0.0012	0.0015	0.0029	0.0127	0.0130	38	
6	0.0085	0.0075	0.0073	0.0068	0.0177	0.0161	33	Dionex IC
Mean	(0.0050)*2		0.0048		0.0171			
Repeatability SD	(0.0004)		0.0004		0.0007		0.0013% in ASTM C1218	
Reproducibi-lity SD	(0.0041)		0.0036		0.0043		0.0037%% in ASTM C1218	

*1. Solution was prepared as 35.45 mg/L.
*2. Use 0.0009 for values reported <0.001 in the analysis.

For CL10 with higher mean chloride content of 0.017%, the coefficient of variation of repeatability and reproducibility are 4.4 and 25% respectively. These are within an acceptable range similar to ASTM C1218 and hence the water-soluble test method gives good precision for aggregates with the AS 2758.1 reportable chloride content.

This draft water-soluble chloride testing method was introduced to Standard Australia CE-012 committee in 2014, in consultation with Standard Australia BD-042 committee for designation as the new Australian Standard AS 1012.20.2. It went to a combined procedure early in 2015 for possible publication around May 2015.

3.3 Conclusion on the proficiency of the two chloride test methods

Both proficiency test programmes focused exclusively on the analysis of chloride content and did not examine the possible variability due to sample preparation technique. The results show that the draft water-soluble test method provides results to the 0.001% accuracy demanded by concrete specifications. The water-soluble test method also gives good precision in terms of both repeatability and reproducibility. However, the AS 1012.20.1 acid-soluble chloride test method has failed to provide the same precision except for the repeatability of aggregate with high chloride content well in excess of 0.01%.

4. Performance limits for concreting materials and concrete

Australian Standards AS 3972, AS 3582 and AS 2758.1 place limits on acid-soluble chloride in cement, SCM and reportable chloride in aggregates respectively. AS 1379 places a limit on total acid-soluble chlorides in the supplied concrete to ensure durability.

There are challenges associated with AS 1012.20.1 acid-soluble chloride determination. The proficiency programme found large variations in the reported results leading to a low precision of the test method. The use of the test method in specifications creates issues in aggregate selection and in determining the risk of steel reinforcement corrosion in hardened concrete. On the other hand, the draft AS 1012.20.2 water-soluble chloride test method has proven to give much improved precision with better repeatability standard deviation than and comparable reproducibility standard deviation to the ASTM C1218 method.

Table 3 Performance limits and corresponding chloride determination methods

Maximum acid-soluble chloride-ion content, percent by mass of cement		Maximum water soluble chloride-ion (Cl^-), percent by mass of cement	
Standard	**Reinforced**	**Standard**	**Reinforced**
AS 1379	0.8 kg/m^3 or 0.20%[a] RC and concrete with tendons. ducts, cast-in inserts, embedded items or other items that require protection.	ACI 318-05 At 28-42 days	0.06, 0.30, [1.00], 0.15 % Prestressed concrete, RC exposed to wet chloride in service, [RC in dry condition in service], Parking structures and those near seawater
ACI 222R-01	0.08, 0.10, [0.20]% Prestressed, RC in wet condition, [RC in dry condition]	ACI 222R-01	0.06, 0.08, [0.15]% Prestressed concrete, RC in wet condition, [RC in dry condition]
European Standard EN 206-1	0.10-0.20[b]% for prestressed 0.20-0.40[b]% for RC 1.00% for plain concrete	Canadian CSA A23.1-94	0.06, 0.15, 1.00 % Prestressed concrete, RC in moist or chloride or both, RC exposed to neither moisture nor chloride
British Standard BS 5328-97	0.10 % for prestressed 0.40 % for RC No limit for plain concrete		
Norwegian Code NS 3420-L	0.6% for RC 0.002% for prestressed		

Note: (a). assumed cement content of 400 kg/m^3.
(b). the class to be applied depends upon the provision valid in the place of use of concrete.

Different international codes and standards have adopted different performance limits for concrete structures. American Concrete Institute (ACI) uses both water-soluble and acid-soluble limits whereas

European and Australian Standards adopt acid-soluble chloride limits. These performance limits and corresponding type of chloride are summarised in Table 3.

It may be prudent for Australian standard AS 1379 and other specifications to consider adopting a water-soluble chloride limit for new concrete to alleviate the low proficiency problem in the acid-soluble chloride determination. A water-soluble chloride limit of 0.6 kg/m^3 for new concrete is recommended for AS 1379.

5. Discussion

In the Australian Standard for acid-soluble chloride content AS 1012.20, no precision statement is available nor is there a stipulation of the accuracy of reporting. The problem affecting the precision of the acid-soluble chloride test (AS 1012.20) has been examined from the viewpoint of the size and sampling method by Forster & Bathgate (2009). The results reported in this paper show that AS 1012.20 test method does not provide a consistently accurate result to 0.001% demanded by concrete specifications. In the case of aggregate with reasonably high chloride content, the test method provides an acceptable repeatability but excessive reproducibility. With the reproducibility standard deviation of 0.0179%, results of two properly conducted tests from two different laboratories on samples of the same material could differ by 0.05% (2.83 x 0.0179%) by mass. This renders the method and its test result to be unacceptable to all parties.

AS 1379 limits the level of acid-soluble chloride in reinforced concrete to be within 0.8 kg/m^3. A typical concrete mix may contain 700 kg/m^3 of sand from 1800 kg/m^3 of combined aggregates. The choice of testing laboratory can contribute a difference of 0.35 kg/m^3 (0.05% x 700 kg) from the sand toward the limit of 0.8 kg/m^3 for concrete which is clearly an unacceptable uncertainty derived from the testing method. If the method is used to determined acid-soluble chloride in hardened concrete, the results of two properly conducted tests from two different laboratories on the same hardened concrete sample could differ by 0.05% by mass of concrete. This amount is almost the chloride threshold associated with potential corrosion of steel reinforcement. Such discrepancy could easily lead to wrong decision regarding the risk of corrosion of steel reinforcement.

On the other hand, the newly developed water-soluble chloride test method has acceptable repeatability and the highest reproducibility standard deviation of 0.0043%, results of two properly conducted tests from two different laboratories on samples of the same material could differ by 0.01% (2.83 x 0.0043%). The choice of testing laboratory can contribute a maximum difference of 0.07 kg/m^3 (0.01% x 700 kg) from the sand toward the recommended water-soluble chloride limit of 0.6 kg/m^3 for concrete which is a more acceptable level of uncertainty derived from the testing method.

6. Conclusions

The lack of precision of the Australian Standard test method for acid-soluble chloride content AS 1012.20.1 has been confirmed and shown to be potentially damaging to decision on the choice of concrete aggregates and the risk of corrosion of steel reinforcement in concrete. The draft AS 1012.20.2 water-soluble chloride test method gives significantly better precision with improved repeatability and reproducibility standard deviation comparable to the ASTM C1218 method. The permissible and reportable water-soluble chloride limits specified for new concrete and aggregate in AS 1379 and AS 2758.1 should also be revised accordingly.

7. Acknowledgement

Cement Concrete and Aggregates Australia (CCAA) acknowledges the collaboration by the following laboratories who participated in the proficiency programmes.

- Sharp and Howells. Bullen, Victoria 3105.
- Sydney Analytical Laboratories Pty Ltd. Seven Hills, NSW 2147.
- SGS Australia Pty Ltd. New Burn, WA 6105.
- SGS Australia Pty Ltd. Rocklea, Brisbane, QLD 4106.
- Boral Materials Technical Services. Baulkham Hills, NSW 2153.
- Queensland Department of Transport and Main Roads. Materials Services.
- RTA Chemical and Materials Laboratory, Auburn, NSW 2144.

8. References:

American Concrete Institute, 'Protection of Metals in Concrete Against Corrosion, Part 1' ACI 222R-01.

American Concrete Institute Committee 222, 'Provisional Standard Test Method for Water-Soluble Chloride Available for Corrosion of Embedded Steel in Mortar and Concrete Using the Soxhlet Extractor', ACI 222.1-96.

ASTM C1218 Standard Test Method for Water-Soluble Chloride in Mortar and Concrete, American Society of Testing and Materials, West Conshohocken, PA, 2008.

ASTM C1152 Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete, American Society of Testing and Materials, West Conshohocken, PA, 2004.

Byfors, K., Hansson, C.M. and Tritthart, J. (1986). Pore solution expression as a method to determine the influence of mineral additives on chloride binding. *Cement Concr. Res*. 16(5), 760-770.

Forster, G. J., and Bathgate, S.N. The Significance of Chlorides in Concrete Trial Mixes. *Proc of Concrete Institute of Australia Concrete Solutions 2009*, Sydney, Australia.

Gaynor, R.D. 'Understanding Chloride Percentages', Concrete International, V.7, No. 9, Sept 1985, pp 26-27.

Glass, G.K. and Buenfeld, N.R., 'The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete', Corrosion Science, V.42, Iss. 2, Feb 2000, pp 329-344.

Hope, B.B., Page, J.J. and Poland, J.S. (1985). The determination of the chloride content of concrete. *Cement Concr. Res*. 15(5) 863-870.

Lamond, J.F. and Pielert, J.H. (1998). Significance of tests and properties of concrete & concrete-making Material. ASTM International, West Conshohocken, PA, USA.

Rogers and Woda (1997). The Chloride Ion Content of Concrete Aggregates from Southern Ontario. Report No. EM-17, Ontario Ministry of Transportation and Communications, Downsview.

Sirivivatnanon, V., Thomas, W.A. & Waye, K. 2011, 'Determination of free chlorides in aggregates and concrete', *Australian Journal of Structural Engineering*, Vol. 12, No. 2, pp.151-158.

Standards Australia. Determination of chloride and sulfate in hardened concrete and concrete aggregates, AS 1012.20, Sydney, 1992.