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Chloride Thresholds and Limits for New Construction

SP-308

Editors:
David Tepke, David Trejo, and O. Burkan Isgor



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Preface

The detrimental influence of chlorides on the corrosion of reinforcing steel in concrete has been widely documented. The literature clearly shows that chloride concentration at the steel level must exceed a critical chloride threshold to initiate active corrosion of reinforcement embedded in concrete. It is now well accepted that this critical chloride threshold is not a unique value, but rather a range that depends on several factors. Regardless, placing concrete with chloride concentrations above the critical chloride threshold for a particular situation would result in active corrosion of the reinforcement and is therefore undesirable. Unnecessarily restrictive limits, however, can lead to preclusion of some otherwise acceptable materials or require use of supplemental materials or alternative mixture designs that may increase costs or impact sustainability. Thus, there is a need from a practical standpoint to establish conservative, yet reasonable, limits so that the effects of corrosion can be managed without undue restrictions. ACI documents place limits on the amount of chlorides that can be incorporated into new concrete – these limits are referred to as the allowable admixed chloride limits.

Documents published by ACI Committees 201 and 222 currently recommend limiting admixed chlorides based on a mass percentage of the portland cement in the concrete mixture. Other documents, such as ACI 318, limit the admixed chlorides based on weight percentage of cement. With the movement of the industry towards greener systems, the inclusion of supplementary cementitious materials (SCMs) as part of the cement could be beneficial. SCMs, however, when used in large quantities, have been reported to decrease the pH of the pore solution, which may lower the critical chloride threshold values. If the critical chloride threshold values for concrete systems containing only portland cement are different than the critical chloride threshold values for systems containing portland cement and SCMs, the published allowable admixed chloride limits may not be applicable. A further complication in establishing values exists due to performance-based cements in which the specific amounts of SCMs might not be known to the specifier.

This special publication (SP), based on two technical sessions held during the Fall 2015 Concrete Convention and Exposition in Denver, CO, November 8-11, 2015, addresses challenges associated with allowable admixed chloride limits, critical chloride thresholds, testing for the critical chloride threshold, binding of chlorides in different systems, and how admixed chlorides influence service life. Authors and presenters from North America and Europe provided a variety of perspectives, experiences, and opinions. Based on the presentations, the open discussion that followed the presentations, and the papers in this SP, evidence indicates that allowable chloride limits should be based on cementitious materials content including both portland cement and SCMs. However, because research on the amount of chlorides required to initiate corrosion in systems containing high SCM replacement levels suggests that there may be upper limits at which the inclusion is appropriate, it was suggested that it may be appropriate to place limits on the replacement percentages of SCMs used for calculations of cement content when determining allowable admixed chloride limits. Although the Denver sessions and the papers in this SP provide a significant move forward on better defining allowable chloride limits and likely allow for refinement of current recommendations in ACI documents, more research is needed.

On behalf of ACI Committees 201 and 222, the editors sincerely thank all authors and presenters for their efforts and contributions to the presentations, open forum, and this SP volume. Special thanks are extended to the peer reviewers of the manuscripts for their constructive comments and recommendations. The editors are also indebted to the ACI staff for their assistance in organizing the sessions, organizing the open forum, and in preparing this volume. The editors earnestly hope that this symposium and SP volume will serve as a valuable resource to those searching for data, guidance, and better clarity on allowable admixed chloride limits in concrete.

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CHLORIDE THRESHOLD VALUES IN CONCRETE – A LOOK BACK AND AHEAD

Ueli M. Angst and Bernhard Elsener

Synopsis: Over the last 60 years, extensive research efforts aimed at determining the so-called chloride threshold value in reinforced concrete. The belief that such a threshold exists is the root of all efforts to measure and model chloride ingress into concrete. This paper addresses the usefulness of this established concept by evaluating the experience available for portland cement systems. Additionally, it is critically discussed whether the concept can be applied to modern materials, particularly SCMs. Finally, suggestions for future research are made.

It is concluded that the pronounced stochastic nature of the chloride threshold currently permits only corrosion prognoses with large uncertainties. It is shown that even the most sophisticated chloride transport model in concrete will not significantly improve this. Instead of refining mass transport models, future research should thus aim at finally understanding the relevant parameters governing corrosion initiation in concrete. There is strong indication that a number of such parameters are overlooked in the current concept of the chloride threshold value. We believe that as long as initiation of chloride-induced corrosion is not fully understood, it does not make sense to continue applying the (unsuccessful) concept of the chloride threshold value to modern materials.

Keywords: Chloride threshold value; Chloride induced corrosion; Critical chloride content; Durability, Reinforcement corrosion; Service life modelling; Supplementary cementitious materials; Sustainability

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INTRODUCTION

In many countries around the world, portland cement has for decades been the most used type of cement to build reinforced concrete infrastructure. In recent years, however, portland cement has increasingly been substituted with supplementary cementitious materials (SCMs). Table 1 illustrates this by means of the example of Switzerland. While for some of these materials there may be positive track records from certain countries – for instance for ground granulated blast furnace slag that has been used in the Netherlands for roughly a century – the diversity of cementitious materials and mineral binders to be used in the future is expected to increase, owing to, amongst others, reasons of local availability of raw materials (Angst et al. 2012). The main motivation for reducing the “clinker factor”, i.e. to increasingly substitute portland cement clinker partially with SCMs, is on the one hand to reduce the environmental impact, particularly by reducing the carbon footprint, and on the other hand to improve the durability. Achieving sustainability clearly not only requires decreasing the environmental footprint of the materials at the time of their production, but to combine this with long and maintenance free service lives of the structures in their actual exposure environments.

Due to the lack of long-term experience on the field performance of modern materials, we are forced to make predictions. This is done based on theoretical reasoning and on accelerated laboratory (or field) testing, believed to provide a basis to extrapolate the short-term behaviour to long-term and field conditions.

Essentially, these efforts consist in adapting concepts established with experience from portland cement and applying them to the new materials. The conceptual understanding of degradation due to chloride-induced corrosion of reinforcing steel in concrete evolved in the second half of the last century and has since then essentially been unchanged. The widespread hypothesis is that the chloride concentration at the surface of the embedded steel is the by far most important parameter, and hence that initiation of corrosion can be predicted by reducing the entire problem to a question of chloride concentrations only. This is illustrated by the extensive research efforts performed over the last 60 years, seeking to determine the so-called *chloride threshold value* or *critical chloride content* (Angst et al. 2009), i.e. to specify a threshold concentration below which, conceptually, there is no corrosion and above which corrosion occurs.

The belief that such a threshold exists is also the root of all research efforts to measure and model chloride ingress into concrete. This issue received considerable research attention over the last decades, and a high number of test methods have been devised internationally for assessing the ability of concrete to resist chloride penetration, as e.g. reviewed in Tang et al. (2012).

Table 1 — Types of cement sold in Switzerland in the years 1996, 2006, and 2015, illustrating the sharp transition from Portland cement to blended cements; data from (CemSuisse).

Cement type	Designation (acc. to EN 197-1)	1996	2006	2015
Portland cement	CEM I	87%	37%	13%
Blended Portland cement	CEM II	11%	60%	83%
Slag cement	CEM III	<1%	<2%	<1%
Other		<2%	<2%	<4%

The consequence of the concept of the chloride threshold value is that materials such as cement types or concrete formulations are commonly regarded as parameters, i.e. that chloride ingress properties and chloride threshold values can be determined by test methods for these different materials in order to predict the time to corrosion initiation.

This paper addresses first the usefulness of this established concept by evaluating the experience available for portland cement systems. Subsequently, it is critically discussed whether the concept can be applied to modern materials, particularly SCMs, and which factors are currently seen to potentially handicap this application. Finally, suggestions for future research are made.

EXPERIENCE FROM PORTLAND CEMENT SYSTEMS

Literature data

Laboratory and field data—In a literature review performed by Angst et al. (2009), the variability of published chloride threshold values was found to be extremely high. Values determined in laboratory studies scattered from almost 0 to more than 8% chloride by mass of binder if all cement types are considered; if only studies with portland cement (excluding low C_3A cements) are considered, the results span still from almost 0 to more than 3% chloride by mass of cement. No systematic trends could be found such as with respect to water/cement ratios, methods of accelerating chloride ingress, storage conditions (e.g. humidity), and corrosion detection methods.

It may also be worth mentioning that within this huge span of reported laboratory chloride threshold values, the results of most individual studies covered only a small fraction of the entire span. In other words, some studies tended to give results in the lower range of the literature span, some were on an intermediate level, and some studies yielded results in the higher end of the literature span. Thus, the entire variability in the literature seems to arise from the combination of different experimental parameters used in each study, i.e. from the measurement method.

Considering data from field exposure sites or from measurements on real structures shows a better agreement between individual reports, but still a large variability. In the 1970s and 1980s, a number of studies reported that chloride threshold values scattered in the range 0.1 to 2% chloride by weight of cement (Stratfull et al. 1975, Vassie 1984, Treadaway et al. 1989). It can be assumed that all of these studies dealt with portland cement.

Figure 1 shows a compilation of literature data providing information on the statistical distribution of the chloride threshold value. Note that data on the probability of corrosion initiation at certain chloride concentrations is scarce, and that not many more such references can be found in the literature. The data shown in Figure 1 as triangles stems from laboratory studies. In the work of Zimmermann (2000) ribbed carbon steel rebars (diameter 8 mm (0.315 inches), length 65 mm (2.56 inches)) were embedded in mortar ($w/c=0.6$). The specimens were immersed in a chloride solution; initiation of corrosion was determined by monitoring the steel potential. In another laboratory study (Breit 2001), similar specimens were used (rebar diameter 10 mm (0.39 inches), length 55 mm (2.17 inches), smooth steel bars; $w/c=0.5-0.6$), but they were not left at their open circuit potential during immersion in chloride solution, but polarized to relatively positive potentials (+0.5 V vs. SHE). Both experimental setups can only mimic reality to a certain extent; differences in this regard have been discussed in (Angst et al. 2011b). Nevertheless, both setups permit to accurately detect corrosion onset and thus, the determined chloride content at the time of corrosion initiation, is considered to represent well the chloride threshold value (under the given conditions). In contrast, the well-known data from field experience reported by Vassie (1984) (bridge structures in the UK) may include larger uncertainties since the time of corrosion initiation was not accurately known. Nevertheless, the results stem from real structures and thus, they are free from artefacts that typically arise from the way specimens are produced and exposed in accelerated laboratory testing (Angst et al. 2009). Figure 1 also shows the distribution of the chloride threshold value indicated in the fib model code for service life design (International Federation for Structural Concrete (fib) 2006), which is based on the data by Breit (2001).

Recent field data from Switzerland—In a recent study by ETH Zurich, a more than 40 years old tunnel in the Swiss Alps was investigated. Cores of 150 mm (5.9 inches) were drilled from within a concrete area of less than 2 m² (10.8 ft²) in size, thus presumably from the same batch of concrete. Each core centrally contained a segment of reinforcing steel. The location of the sampling area was selected based on condition assessment of the structure in order to ensure that the reinforcement was still in passive condition. Additional measurements also indicated a negligible level of chloride concentrations at the steel depth (in this area) and that the carbonation front was still far from the steel depth.

The samples were transferred to the laboratory and underwent a procedure of sample preparation. This included establishing a cable connection to the rebars, special actions to prevent the cut faces of the rebars from initiating corrosion (by applying a dense mortar), and subsequent coating of the lateral faces of the core with an epoxy-resin. The samples were then subjected to wetting/drying exposure in the laboratory (with stepwise increasing chloride concentration in the exposure solution) and the potential of the rebars was monitored vs. a reference electrode. Detection of corrosion initiation was based on a criterion related to a drop in potential as established in previous work (RILEM, Angst et al. 2011c). At the time of corrosion initiation, the chloride content at the steel surface was measured, thus yielding the chloride threshold value. A more detailed description of the procedure can be found in (Wagner et al. submitted to advisory commission). The advantage of the used approach lies in ensuring realistic specimens thanks to taking them from real structures (mature concrete, realistic conditions at the steel/concrete interface, etc.) and combining them with the accuracy of laboratory measurement methods for detecting corrosion initiation. The results are shown in Figure 1, denominated “Swiss field data”.

It is evident from Figure 1 that the field data (Vassie’s results and Swiss data) scatters somewhat more than the laboratory data (Zimmermann, Breit). This may be explained by the higher variability in material properties in real structures compared with laboratory samples that are usually cast, compacted, cured, etc. under more controlled conditions. One can also see that the field data scatters more than what is used in the fib model code for service life design. Nevertheless, one may argue that all the data in Figure 1 indicates a probability of corrosion initiation of approx. 20% at chloride contents in the range 0.3–0.5 % by cement weight. This agrees also rather well with the famous threshold value of 0.4% chloride by weight of cement suggested in the 1960s by Richartz (1969).

A second observation from Figure 1 is that the chloride content associated with corrosion initiation in reinforced concrete is not a unique threshold value, but must be described with a statistical distribution. The field data suggests that steel may be corroding or still passive at chloride contents ranging from 0.2% chloride by weight of cement to more than 1.5% chloride by weight of cement. Towards the lower end of this range, the probability for corrosion is

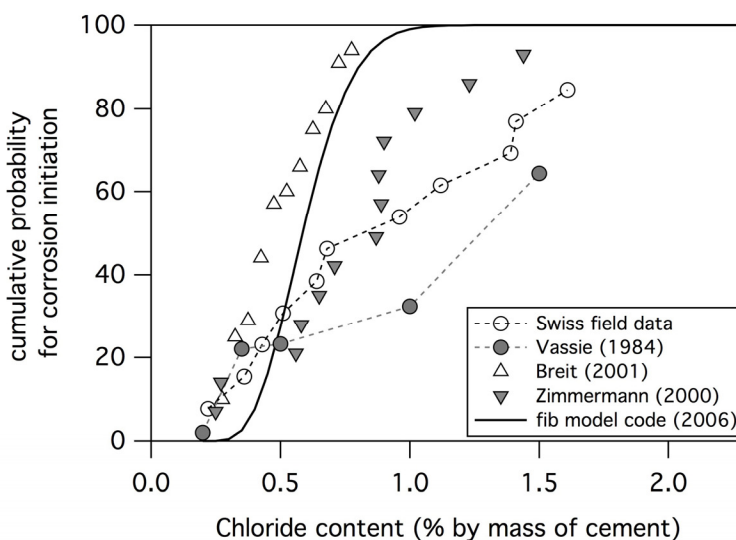


Figure 1 — Literature and own data on the statistical distribution of chloride threshold values in portland cement systems. Circles = field data, triangles = laboratory data; solid line = distribution suggested in the fib model code for service life design; see text for explanations.

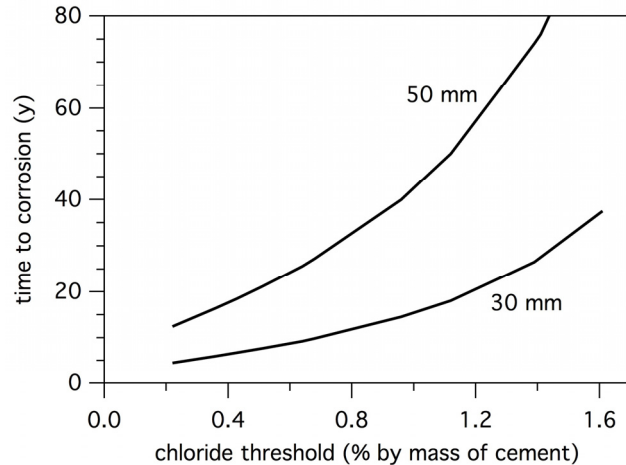


Figure 2 — Example of forecasting the time to corrosion by a simple chloride ingress model (see text for explanations) for two different cover depths and as a function of the assumed chloride threshold value (deterministic model).

low, with increasing chloride concentrations, the probability for corrosion increases. Even at values as high as 1% chloride by cement weight, the field data suggests that the probability for corrosion is not much higher than 50% (in portland cement systems).

Implications for service life modelling

The fact that the distribution of the chloride threshold value spans over such large ranges has major implications for projecting the time to corrosion initiation in service life modelling. This may be illustrated with a simple model of chloride ingress, based on Fick's second law of diffusion and the well-known error function solution, as described e.g. in the fib model code for service life design (International Federation for Structural Concrete (fib) 2006). The chloride concentration in the concrete $c(x,t)$ as a function of depth x and time t can be expressed as follows:

$$c(x,t) = c_o + (c_s - c_o) \left\{ 1 - \operatorname{erf} \frac{x}{2\sqrt{D_{app} \cdot t}} \right\} \quad (1)$$

Assuming a surface chloride concentration c_s of 3% chloride by weight of cement, a negligible initial chloride content c_o in the concrete, and a constant apparent diffusion coefficient D_{app} of $1 \times 10^{-12} \text{ m}^2/\text{s}$, the chloride content in the concrete can be predicted for different cover depths. For a given chloride threshold value, it is then possible to predict the time to corrosion initiation. Note that this example is a simple deterministic model, where any variability in the input parameters, e.g. in the chloride diffusion coefficient, the surface chloride concentration, the cover depth, etc. is neglected.

Figure 2 illustrates the wide range in predicted time to corrosion that results from different chloride threshold values. Note that the chosen range in chloride threshold values corresponds to the one of the field data shown in Figure 1. Depending on the actual value assumed for the chloride threshold, for a cover depth of 50 mm, the projected time to corrosion may be as low as 15 years or higher than 80 years.

It is important to recognize that even small differences in the assumed chloride threshold value have a strong impact on the resulting time to corrosion (and thus on the predicted service life). This is due to the fact that particularly at higher cover depths and towards later stages (typically after a few decades), the increase in chloride concentration vs. time becomes moderate. Note that this marked sensitivity of the prediction to the assumed chloride threshold becomes even more pronounced the higher the level of chloride threshold values.

Probabilistic considerations—By taking into account the probability distribution of the chloride threshold (as shown in Figure 1) the modelled time to corrosion may also be presented differently, namely by plotting the probability at which corrosion has initiated after a certain numbers of years. This is shown in Figure 3.

For instance, at a cover depth of 50 mm, there is a 10% probability that corrosion has initiated after approx. 14 years, after only 5 more years (i.e. after 19 years), this probability has already increased to 20%. However, after a service life of 100 years, there is still a probability of approx. 20% that no corrosion has initiated. Note that the probability for corrosion increases rather drastically at early ages (such as a jump in 10% probability from 14 to 19 years for 50 mm cover depth). This is the direct result of the relatively steep increase in chloride concentrations at young exposure times combined with the fact that the lower tail of the probability distribution of the chloride threshold value spreads down to relatively low chloride concentrations (in the range of 0.2% chloride by cement weight). This presents a potential problem, since the acceptable probability for corrosion, is usually chosen in the lower end, such as 5%, 10%, or eventually 30%. Obviously, the model uncertainties are largest in this range.

Note that in this example, the projection of the chloride content in the concrete at the steel surface was done deterministically, i.e. with fixed input parameters. Recognizing that also these parameters are variable and thus describing them with help of a statistical distribution, which is common practice, would add even further uncertainties to the model predicting the time to corrosion initiation.

Large uncertainties in current modelling—In any case, the calculations plotted in Figure 2 and Figure 3 – based on realistic input parameters for chloride ingress modelling and on field data for the chloride threshold value – clearly reveal the large uncertainties inherent to current predictive modelling. From an engineering perspective, one may question the benefit of a prognosis stating that corrosion will initiate sometime between 15 and 100 years after construction. It is time to admit that the established, state-of-the-art approach to forecast the time to corrosion has a very weak predictive power. As a result of the high inherent uncertainties of this approach, engineers, owners, or infrastructure managers are forced to take highly conservative decisions, which in turn implies high costs to our society.

Considering corrosion initiation in concrete as a mere question of chlorides does and will only permit corrosion prognosis with a very low level of confidence. Having in mind the vast statistical dispersion of the chloride threshold value (Figure 1), it may also be important to recognize that even the most sophisticated model to predict chloride ingress into concrete will not significantly improve this. In our opinion, the concept of the chloride threshold value needs to be replaced or enriched with a more refined approach capable of taking into account all other dominant and relevant influencing factors.

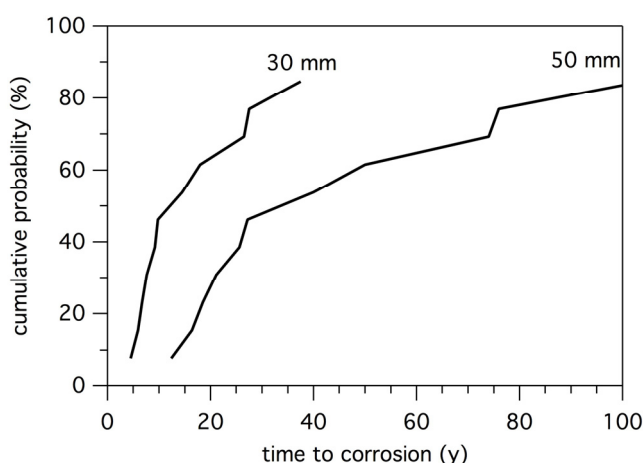


Figure 3 — Example of forecasting the time to corrosion by a simple chloride ingress model (see text for explanations) for two different cover depths. The plot details the probability at which corrosion has initiated after a certain numbers of years, assuming a distribution of the chloride threshold value according to the “Swiss field data” shown in Figure 1.

APPLYING THE ESTABLISHED CONCEPT TO MODERN MATERIALS

The concept of the chloride threshold value implies that any material characteristics – such as the type of cement, concrete mix proportions, the steel grade, etc. – can be regarded as a test parameter that influence:

- 1) The kinetics of chloride ingress into the concrete
- 2) The chloride threshold value

Ideally, these influences can be tested and quantified in order to provide the input data needed in predictive modelling. Concerning the kinetics of chloride penetration, there seems to be some literature agreement about the effect of certain concrete mix related parameters. It is well established that decreasing the w/c ratio and/or using supplementary cementitious materials (at least some of them) can create a denser, more tortuous concrete pore system and thus improve the resistance against chloride penetration (Bertolini et al. 2013). This can also reasonably be quantified by experimentally determining the chloride diffusion coefficient and the ageing coefficient of the material under study if a Fick's second law of diffusion type of chloride ingress model is used (Tang et al. 2012). Alternatively, for more sophisticated mass transport models, different parameters need to be quantified (e.g. (Marchand and Samson 2009, Tang et al. 2012)). Nevertheless, the current state-of-the-art permits relatively well predicting chloride penetration through concrete for different systems.

Concerning the second point named above, the chloride threshold value, the literature documents a considerable number of attempts to experimentally determine the chloride threshold value for fly ash concrete, slag concrete, etc. or for different w/c ratios (Angst et al. 2009). Despite this, the current state-of-the-art offers very little convincing agreement on these parameters, particularly concerning the type of binder. This may be illustrated with help of the example of fly ash: While some authors reported decreasing chloride threshold values with increasing fly ash contents (Thomas 1996, Oh et al. 2003), others found increasing chloride threshold values for concrete with fly ash (Schiesl and Breit 1996) or no influence at all (Alonso et al. 2002). This literature disagreement was in (Angst et al. 2009) explained by the huge differences in experimental approaches used by the different authors, and the unfortunate fact that some of the parameters inherent to experimental setups have a more pronounced influence on the resulting chloride threshold value than the variables under test.

Potential problems with the established concept

A variety of parameters – other than the chloride concentration – have been observed to play a role in corrosion initiation in chloride contaminated concrete. This includes the pH of the concrete pore solution, the reinforcing steel potential, and the conditions at the steel/concrete interface. The following sections outline a few potential issues arising from the use of SCMs that may complicate the application of the concept of the chloride threshold value to these systems.

Alkalinity of the concrete pore solution—The introduction of non-portlandite binders has strongly increased the diversity of the pore solution chemistry in concrete. One important factor is that the pH of systems with SCMs is typically lower than the pH in portland cement systems. Additionally, also the pH buffer capacity is generally depressed as a result of the reduction (or elimination) of the calcium hydroxide reserve. This calcium hydroxide reserve is one of the main reasons for the corrosion inhibiting nature of portland cement systems (Bäumel 1959, Page 1975). From experiments in aqueous solutions, it is well known that the chloride concentration needed to initiate corrosion increases with increasing pH (Venu et al. 1965, Hausmann 1967, Gouda 1970). This is reflected in the suggestion of expressing the chloride threshold value as the ratio chloride/hydroxyl ions (Hausmann 1967). Nevertheless, it is still common practice to express the chloride threshold value as percentage of chloride by weight of binder also for blended cements, thus neither the pH nor the pH buffer capacity are directly taken into account.

Chloride binding capacity—SCM containing concretes typically have a different ability to bind chlorides than ordinary portland cement concrete (Larsen 1998). Thus, when measuring (or predicting) total chloride contents in the concrete, the relative fractions of bound and free chlorides are different in modern systems as compared to traditional portland cement concrete. This directly affects the ratio chloride/hydroxyl ions in the concrete pore solution and thus initiation of corrosion.

Establishing stable pitting corrosion—The reduction in pH buffer capacity in the presence of SCMs and the differences in chloride binding capacity likely play a role in establishing stable pitting corrosion. It is well known that

initiation of pitting corrosion occurs as a sequence from pit nucleation to metastable pitting to stable pit growth (Burstein et al. 1993). For steel in concrete, stable pit growth may in many cases not directly establish; due to insufficient supply of (free) chloride ions to the nucleated pit, the steel may undergo several repassivation events before stable pitting is established (Angst et al. 2011a, Angst et al. 2011c). The factors governing this in concrete are the availability of free, thus mobile hydroxyl and chloride ions in vicinity of the nucleated pit. Both these species migrate and diffuse into the pit in a competitive manner. For stable pit growth to be achieved, it is needed that transport of chloride becomes dominant over transport of hydroxyl ions (Angst et al. 2011a). After a certain time, these species will be transported from more remote areas; additionally they will also be supplied by dissolving solid phases of the cement paste (e.g. calcium hydroxide) and by releasing bound chlorides from the concrete at the pit mouth. Although it appears that the pH buffer capacity and the chloride binding capacity of the concrete are decisive parameters in this regard, their influence is currently not well understood and can at present not yet be taken into account in predictive models.

Sulphides and other species in the concrete pore solution—From experience with slag cements, it is known that the presence of sulphides can strongly depress the potential of the embedded reinforcing steel. In (Garcia et al. 2014) for instance, potentials more negative than -500 mV SCE were reported for slag containing concrete (in the absence of chlorides). It is known that more negative steel potentials can largely increase the chloride concentration needed to initiate corrosion (Alonso et al. 2002, Angst et al. 2009). Different hypotheses have been suggested to explain the effect of the sulphides (from the slag) on the steel potential. Macphee and Cao suggested that oxidation of the sulphides consumes the oxygen in the concrete pore solution, and thus, the lack of oxygen is seen as the cause of the negative steel potential (Macphee and Cao 1993). Other authors suggested that different oxidation/reduction couples involving sulphides determine the steel potential, e.g. (Holloway and Sykes 2005). In any case, there is a lack of thorough understanding of the processes occurring in the presence of species such as sulphides in the concrete pore solution and how they affect corrosion initiation.

Steel concrete interface—It is recognized that voids, bleed water zones, cracks, pre-existing rust layers, mill scales, etc. can act as preferable corrosion initiation sites. However, the accurate mode of action of these characteristics in promoting corrosion initiation is currently not well understood. Nevertheless, there is indication that some characteristics at the steel/concrete interface play a highly dominant role in corrosion initiation (Angst et al. 2009). It is the aim of the recently established RILEM technical committee SCI (RILEM) to compile in detail the available literature and knowledge in this field and to identify the areas, where more research work is most urgently needed. Gaining fundamental and mechanistic understanding concerning the influence of individual characteristics at the steel/concrete interface is important also in the context of SCMs as it is well known that blended cements can greatly modify some of the properties of the steel/concrete interface.

Corrosion propagation stage—Finally, it is common practice to understand the service life of a structure as the time to corrosion initiation. This is primarily due to the fact that chloride-induced and thus localized corrosion is often associated with relatively high rates of loss of steel cross sectional area, which may give rise to critical conditions from the viewpoint of serviceability or structural safety within relatively short time (Bertolini et al. 2013). Thus, the propagation stage may indeed in many practical cases be short in comparison with the initiation stage. Another reason for conservatively understanding the end of the service life as the time to corrosion initiation can also be found simply in the lack of reliable models for the corrosion propagation stage (Raupach 2006, Otieno et al. 2011, Hornbostel et al. 2013).

Nevertheless, in non-portlandite systems, corrosion may in principle initiate relatively early and at lower chloride concentrations than in portland cement systems (due to the lower pore solution pH), but the rate of steel mass loss may still be lower. One possible reason for this is the decreased mass transport in many of the modern systems, which can potentially slow down all the different reaction steps of the corrosion process (e.g. the cathodic reaction by limiting oxygen access (Hassan et al. 2000), the anodic reaction by limiting mass transport at the anode (Page and Havdahl 1985), the macro-cell current flow in the bulk concrete (Raupach 1992), etc.). Thus, for concretes containing SCMs it may be even more important than for portland cement concrete to include also the propagation stage in service life models. Continuing to neglect this may not only lead to highly conservative predictions, but also be misleading when comparing the durability (and sustainability) of different modern and traditional binders.

SUGGESTIONS FOR FUTURE RESEARCH

From the previous sections, it is apparent that many questions regarding the mechanism of corrosion initiation of reinforcing steel in concrete are still open. We believe that as long as we do not understand the governing factors for corrosion initiation in chloride contaminated concrete it does not make sense to continue applying the (unsuccessful) concept of the chloride threshold value. Instead, research is urgently needed to clarify some fundamental issues. Only this will allow for a real breakthrough in forecasting the durability of concrete structures.

From the current state-of-the-art it is known that the pH, the pH buffer capacity, and the chloride binding capacity are important parameters. Models to forecast corrosion could thus be improved when they are capable of taking into account the free chloride ion concentrations and the pH of the concrete pore solution rather than only the total chloride content in the concrete. However, particularly for condition assessment of existing structures, there are no feasible methods to accurately and reliably determine the free chloride ion concentrations and the pH. Also for durability predictions of new structures, to be designed with novel materials, accurately modelling the pore solution chemistry during long-term field exposure is a complicated task, also because the experimental validation is not straightforward.

Future research should thus address the following issues:

- Models capable of predicting the pore solution chemistry (rather than only the chloride concentration) during long-term field exposure, and capable of taking into account the release of bound chlorides and the changes in pH at the pit mouth during early, metastable stages of pitting corrosion are expected to significantly improve the accuracy of prognoses of the time to reach stable pitting corrosion (thus the corrosion initiation stage).
- Reliable methods for the determination of free chloride and hydroxyl concentrations in the concrete pore solution, particularly also methods suitable for measurements on-site. This will permit to validate predictive models.
- The effect of sulphides on corrosion initiation needs to be understood in more detail, as there is indication that these cannot be neglected in corrosion prognoses. The same applies to other potential differences in pore solution chemistry of concretes made with SCMs.
- There is an urgent need to understand the role of individual characteristics at the steel/concrete interface. Their influence needs to be clarified and mechanistically understood as only this can lay the basis to develop novel predictive models taking into account the relevant parameters.
- Mechanistic models of corrosion propagation in concrete in order to replace to current, largely empirical models. This will permit taking into account the corrosion propagation stage that may form a substantial part of the service life of concretes made with SCMs.

CONCLUDING REMARKS

This paper discussed the established concept of the chloride threshold value by evaluating the experience available for portland cement systems. Additionally, potential issues arising from the use of SCMs that may complicate application of this concept to these systems were highlighted. The following major conclusions are drawn:

- The chloride threshold inherently exhibits stochastic variability and cannot be treated as a deterministic threshold value. Both field and laboratory data indicate that the probability distribution for corrosion initiation covers a wide range of chloride concentrations – even for a specific concrete or structure and when determined with one unique test method.
- The implication of the pronounced stochastic nature of the chloride threshold is that corrosion prognoses can currently only be made with large uncertainties. This was in this work illustrated with help of an example, considering state-of-the-art data on the distribution of the chloride threshold value.

- From this example, it became also apparent that even the most sophisticated model to predict chloride ingress into concrete will not significantly improve this. Instead of focusing on developing more advanced mass transport models, we thus suggest that future research efforts should aim at finally understanding the relevant parameters governing corrosion initiation in concrete.
- There is strong indication that corrosion initiation in concrete can be significantly affected by a number of parameters that are overlooked in the current concept of the chloride threshold value. Thus, considering corrosion initiation in concrete as a mere question of chlorides does and will only permit corrosion prognoses with a very low level of confidence. Only if the concept of the chloride threshold value can be replaced (or at least enriched) with a more refined approach capable of taking into account all relevant factors influencing corrosion initiation, can the current large uncertainties in predictive modelling be reduced.
- Finally, corrosion initiation and propagation are likely to be mechanistically different in concrete made with SCMs compared to portland cement. This handicaps applying the established (largely unsuccessful) concept of the chloride threshold value to modern binders. There is thus an urgent need for fundamental and mechanistic understanding of the relevant influences.

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CONFUSION ON CHLORIDE LIMITS IN SPECIFICATIONS THAT CHALLENGE THE INDUSTRY

Colin L. Lobo

Synopsis: Chloride limits in concrete are intended to ensure that composition of concrete mixtures do not cause corrosion of reinforcement. This paper provides a brief overview of the requirements in industry standards and discusses some of the test methods used for chloride limits. Estimation of total chloride content in concrete mixtures calculated from the materials and mixture proportions is outlined. It is suggested that the calculated chloride content is a conservative estimate of the available chlorides for corrosion and can be used as an alternative to testing for water soluble chlorides in concrete. The results of a survey of ready mixed concrete producers indicate that chloride limits in concrete are not often required or enforced. Requirements in specifications for concrete vary considerably, are not consistent with Code requirements and often result in contradictory interpretation and requirements.

Keywords: Building code; Chlorides; Corrosion; Durability; Exposure classes; Specification; Specification limits.

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INTRODUCTION

Corrosion of reinforcing steel in concrete is a significant contributor to the deterioration of infrastructure that includes bridges, buildings, pavements and other structures in a wide range of environments. Reinforcing steel is naturally passivated from corrosion when embedded in the highly alkaline environment in concrete. Corrosion initiates when a threshold chloride concentration is exceeded at the reinforcing steel or the concrete cover has carbonated to a level that the alkalinity is reduced to negate the passivation. Industry standards attempt to minimize corrosion by ensuring good quality concrete with adequate cover to extend the time it takes for the transport of chloride ions to the reinforcing steel, minimize cracking, use of corrosion inhibiting admixtures, and to set limits on internal chlorides in concrete from the materials used to make it. In general, good quality concrete is resistant to carbonation and the emphasis in industry standards is on chlorides.

The Building Code (ACI 318-14) defines exposure classes for corrosion protection of reinforcing steel and establishes requirements for concrete used in reinforced concrete members assigned to these exposure classes. These requirements are incorporated in specification format in ACI's reference specification (ACI 301-10). For structural members exposed to an external source of chlorides, the concrete mixture has to be developed with a low w/cm to reduce the rate at which external chlorides migrate to the reinforcing steel. Typically these impact structural members in marine construction or exposed to the application of deicing chemicals that are typically chloride-based.

For all structural members, there are limits on internal chlorides for the concrete in the Building Code (ACI 318-14). The limits vary depending on the exposure class assigned to the member. A lower conservative limit is set for prestressed concrete regardless of the exposure condition because of the dire consequences to structural safety if prestressing strands corrode. The chloride limits are determined on the basis of tests performed on concrete at an age between 28 and 42 days. The water-soluble chloride limits are stated on the basis of percent by mass of cement. With the evolution of more sustainable concrete mixtures with higher quantities of pozzolans and slag, the chloride limits stated on the basis of cement poses a problem for the industry as the limits are considerably lower for these mixtures. While it is recognized that concrete materials are the source of internal chlorides, industry standards do not impose chloride limits on the materials. One exception is an optional limit on mixing water if a non-potable source is used (ASTM C1602).

It is recognized that some of the chlorides introduced from the materials are chemically bound by the cement hydration products and will not be available in the concrete pore solution to initiate corrosion. Carbonation releases some of the bound chlorides to make it available for corrosion (ACI 222R-01). If the chloride content of the concrete materials is known and the total chloride content of concrete is calculated based on the mixture proportions, it can be assumed that the water-soluble chlorides measured on the concrete will be somewhat lower than that calculated. Thereby, if the calculated chloride content of concrete is less than the Code limits, it is reasonable to assume that the concrete will comply with the water-soluble chloride limits when tested. Internal chlorides in concrete mixtures also have other effects on the rate of corrosion (ACI 222R-01).

NRMCA provides simplified guidance to concrete producers on chloride limits and much of the discussion in this paper is based on that reference (NRMCA 2014, Gaynor 1983).

MEASUREMENT OF CHLORIDES

As indicated earlier, not all of the total chlorides in hardened concrete contribute to corrosion. Some of the total chlorides in hardened concrete are chemically bound in hydration products and only a portion of the total chlorides, perhaps 50 to 75%, continue to exist in the concrete pore solution and thereby available to initiate corrosion of reinforcement (ACI 222R-01). For that reason, the Building Code (ACI 318-14) establishes limits on the basis of measurements using the water-soluble test. The acid-soluble test measures the total chlorides. This method may be used to measure the chlorides in solid ingredients used in concrete mixtures.

ASTM C1218 - Water-Soluble Chloride in Mortar and Concrete

For determining the water soluble chloride in concrete for new construction, the test involves making concrete cylindrical specimens, curing them for at least 28 days and then obtaining powder samples from the concrete specimen before an age of 42 days. Some duration of time is required to allow for adequate hydration of cementitious materials that can encapsulate some of the chlorides in the hydration products. A composite powder sample should be prepared from different portions of the specimen so that it is representative. The powder sample tested is about 10 g (0.02 lb) and it is finer than the 850- μ m (No. 20 sieve). The powder sample is boiled in water for 5 minutes and allowed to stand for 24 hours. The water is then tested for dissolved chlorides and this is reported as a percent of the cement or of concrete if the cement content is not known. Generally, the water-soluble chloride content is measured on concrete and not on concrete materials.

ASTM C1152 – Acid-Soluble Chloride in Mortar and Concrete

This test involves digesting the same type of powder sample of hardened concrete in dilute nitric acid. The solution is then tested for chloride content. This chloride content is reported as a percent of the weight of the material being analyzed. This method can be used for concrete materials even though the method does not specifically state that.

ASTM C1524 – Water Extractable Chloride in Aggregate (Soxhlet Method)

This test was developed because some aggregates have a higher quantity of background chlorides when measured by the acid soluble method on powder samples. Since these chlorides are bound within the aggregate minerals they are not available in concrete to contribute to corrosion. The method extracts chlorides from non-pulverized material using the Soxhlet apparatus. The method involves boiling water that condenses and drips on to the sample to saturate it and extract the available water-soluble chlorides. The chloride content of the water is measured. The method has been used to measure the chlorides in non-pulverized concrete samples with low reproducibility. This test was developed primarily for dolomitic limestone found in southern Ontario, New York, northern Michigan and the Chicago area (Whiting, 1997). The method is not intended for marine aggregates or those that contain absorbed chloride in the aggregate pores.

SOURCES OF INTERNAL CHLORIDE

Internal chlorides in concrete originate from the materials used. There are no limits on chlorides for the ingredients used in concrete. Mixing water is one exception; there is an optional limit for non-potable water if used. In most cases, the chloride content of materials used to make concrete are not measured or reported by the supplier. Project specifications often include a chloride limit on admixtures. Eventually it is the chloride limits in concrete that govern.

- a. **Cementitious Materials** - Generally, the total chlorides in portland cement will be less than 50 to 100 ppm.

Chlorides in slag cement and fly ash should be similarly low. The chloride content of cementitious materials is typically available from the supplier. It is being proposed that chloride content of portland cement be reported on the mill test report, but with no specification limit. The chloride content of portland or blended cement will typically be measured by X-ray fluorescence; a rapid method that is typically used to determine the chemical composition of cement.

- b. **Aggregates** - Total chloride content of aggregates will vary greatly depending on the aggregate source. Marine aggregates, especially sand, that have not been properly washed can contribute a significant quantity of water soluble chloride if used in concrete. Total chlorides in certain dolomitic aggregates from quarries in Chicago and Ontario are as high as 0.1 to 0.15 percent by weight of aggregate. This results from the nature of its formation in shallow oceanic environments. Aggregate suppliers from these sources generally provide a statement indicating the successful service history and use of these sources. Most aggregates will have total chlorides less than 0.025 percent by weight of the aggregate. Chlorides in aggregates tend to be bound within the minerals and are not available as water soluble chlorides. However, when aggregates or concrete are crushed to a fine powder for the purpose of testing, these bound chlorides will be measured. It may also be more appropriate to measure the water-soluble chloride content of aggregates in their as-used form, rather than crushing to powder and measuring the acid-soluble chloride content. This would better represent the chloride contribution of aggregate as used in concrete mixtures.
- c. **Water** - Drinking water standards typically set a maximum chloride ion limit of about 250 ppm. Chloride content in city water is generally less than 50 ppm. The chloride content of other non-potable sources of water should be measured. ASTM C1602 establishes an optional limit on chlorides in mixing water (ASTM C1602-13). The limits are 500 ppm for water used in prestressed concrete and 1000 ppm for reinforced concrete or concrete in contact with aluminum embedments or galvanized metal forms. At 1000 ppm, the chloride content from mixing water in concrete amounts to about 0.05% by weight of cement. The chloride content in wash water in concrete plants is generally much less than 1000 ppm, unless concrete containing chlorides is washed out into wash water basins or reclaimers.
- d. **Admixtures** – Use of calcium chloride-based set accelerating admixtures is the primary source of chlorides from admixtures. Calcium chloride is a very effective accelerating admixture but the contribution of chlorides requires its use to be limited in reinforced concrete and prohibited from use in prestressed concrete. The chloride content in non-chloride water-reducing admixtures will generally be between 100 and 800 ppm. Where calcium chloride is used to offset retardation in some water-reducing admixtures to make it set neutral the admixture might contain as much as 200,000 ppm chloride ion. Since the quantity of admixtures used is rather small, the chloride contribution in a concrete mixture is also small. At this concentration an admixture dosage of 3 mL/kg (5 fl.oz./100 lb) of cement results in a total chloride ion concentration of approximately 0.06 percent by weight of cement.

Calculation of Total Chloride in Concrete

Table 1 illustrates the calculation of chloride content in concrete when the chloride content of the materials is known (NRMCA 2014). The chloride contents of the materials are assumed and should not be considered as typical.

As indicated earlier, it can be assumed that the water-soluble chloride in concrete will be about 25 to 50% lower than the calculated value of total chlorides because of being chemically bound in hydration products.

Table 1. Example Calculation of Total Chloride Content in Concrete

Ingredient	Mixture proportion*, lb/yd ³	Total Cl ⁻	Calculation	Total Cl ⁻ , lbs.*
Cement	600	0.005%	$(0.005 \div 100) \times 600$	0.03
SSD Sand	1150	0.01%	$(0.01 \div 100) \times 1150$	0.115
SSD Coarse Agg	1800	0.106%	$(0.106 \div 100) \times 1800$	1.908
Water	280	250 ppm	$(250 \div 10^6) \times 280$	0.07
Admixture	5 oz*	800 ppm	$(800 \div 10^6) \times 5 \times 6 \times (1/16)$	0.0015
Total Cl ⁻ in 1 cubic yard				2.1245
Total Chloride, % by weight of cement $\left(\frac{2.1245}{600}\right) \times 100$				= 0.354 %

* 1 lb/yd³ = 0.59 kg/m³; 1 lb=0.4536 kg; 1fl.oz = 29.6 mL

CHLORIDE LIMITS FOR CONCRETE

The Building Code sets requirements for chloride limits in concrete depending on the exposure to the environment. Chloride limits for concrete were first established in the 1983 Building Code. Currently, ACI 318 defines durability exposure classes (EC) that the design engineer has to assign to concrete structural members. Assigned exposure classes for structural members establish requirements for concrete. These requirements are also reflected in ACI Specification (ACI 301-10).

The chloride limits in ACI 318 and ACI 301 are provided in Table 2. ACI Guide to Durable Concrete (201.2R-08) and corrosion document (ACI 222R-10) provide guidance (not requirements) on chloride limits in concrete. ACI Committee 201 refers to the guidance of ACI Committee 222. The chloride limits suggested in ACI 222 are based on research on the threshold chloride concentration to initiate corrosion and are more conservative than those stated in ACI 318 and ACI 301. The reasoning for the more conservative recommended limits is discussed (ACI 222R-01). The recommendations on chloride limits by ACI Committee 222 are provided in Table 3. If the limits of ACI Committee 222 are invoked in a project specification, these will essentially prohibit the use of admixtures that contain any significant amount of chlorides.

The Code for Environmental Structures uses the same limit as ACI 318 for prestressed concrete but a more conservative single limit of 0.10 percent water soluble chloride by weight of cement for reinforced concrete. ACI Committee 350 states that this more conservative limit is required for environmental engineering structures *due to their greater susceptibility to corrosion of metals, when experiencing prolonged exposures to chloride-saturated solutions* (ACI 350-06).

Note that chloride limits in ACI standards and guides are stated on the basis of percent by weight of portland cement and not cementitious materials. Thereby, concrete mixtures that contain fly ash, slag cement, and silica fume are *penalized* on this basis. Efforts continue to change the chloride limits to the basis of cementitious materials as they are in the Canadian and European standards.

In the past, the Building Code permitted the calculation of chlorides from the concrete mixture proportions to determine whether concrete met the chloride limits, as illustrated in Table 1. Currently ACI 318 requires the water soluble chloride content in concrete mixtures be measured by ASTM C1218 at an age between 28 and 42 days. The

commentary (ACI 318R-14) discusses the option of calculating chloride, but the Code requirement for testing governs. Calculating the chloride content can provide a concrete producer a conservative estimate of the water soluble chloride that might be measured by testing and to decide whether changes to the materials and mixture proportions are needed prior to a submittal. Considering the wide variety of concrete mixtures developed for various applications by ready mixed concrete producers, if testing for chlorides on concrete is enforced, this represents a considerable expense. The alternative to document calculated chloride contents would make this less onerous, especially when the chloride contents are considerably lower than the specified or Code limits. A code change proposal to permit calculation of chlorides, in lieu of testing, has been submitted for letter ballot to Committee 318.

Table 2: Chloride Limits in ACI 318 & ACI 301

EC	Description	Max water-soluble Cl^- , % wt of cement	
		Reinforced	Prestressed
C0	Concrete dry or protected from moisture	1.00	0.06
C1	Concrete exposed to moisture but not to external source of chlorides	0.30	0.06
C2	Concrete exposed to moisture and an external source of chlorides from deicing chemicals, salt, brackish water, seawater, or spray from these sources	0.15	0.06

Table 3. Chloride Limits for new construction in ACI 222R and ACI 201.2R

Category	Chloride (Cl^-) limit, % wt of cement	
	Acid-soluble ASTM C1152	Water-soluble ASTM C1218
Prestressed concrete	0.08	0.06
Reinforced concrete in wet condition	0.10	0.08
Reinforced concrete in dry condition	0.20	0.15

INDUSTRY SURVEY

NRMCA conducted an informal survey of ready mixed industry companies on chloride limits and testing requirements they see in project specifications (NRMCA 2015). Responses were received from about 50 small and large companies supplying concrete in most regions of the US for different types of structures or applications. The questions are listed below and responses are summarized. There were considerable differences in the requirements and enforcement of chloride limits in specifications.

Do you have to do testing for water-soluble chlorides in concrete as required by specifications? How often do you do these tests?

Responses varied from never to very rarely to several projects. Many producers perform tests at least bi-annually to maintain documentation when requested. Requirements for test results on water-soluble chlorides in accordance with ASTM C1218 are common for high-rise buildings in larger metropolitan areas, parking and environmental engineering structures. Testing is required by some design firms involved in these types of projects. In smaller rural markets, the requirement to test is not common.

Producers also reported a range of chloride limits in specifications. The limit for prestressed concrete (0.06%) is sometimes invoked for cast-in-place reinforced concrete and for post-tensioned construction. While post-tensioned concrete is considered prestressed concrete, the relevant question is whether the chloride limits should apply if the concrete does not come in contact with the tendons. ACI 318 establishes limits for post-tensioning grout. Many limits on measured water-soluble chlorides seen in specifications are not consistent with those stated in ACI 318 or based on assigned exposure classes as in the Building Code. The ACI 350 limit of 0.10% is sometimes seen in specifications for buildings. Some producers indicate that their tested (and calculated) values on chlorides are very low and considerably less than the Code limits. Many engineers accept this as a basis to waive testing for specific projects. It was also reported that many specifications only state limits on concrete materials, most commonly on chemical admixtures. This is easy to document since this information is available from the admixture suppliers on all products. Test reports on chloride tests often report results on the basis of percent by mass of cement, percent by mass of total cementitious materials, and percent by mass of concrete.

Roughly what percentage of specifications requires this testing?

Responses varied by region. Chloride limits were seen in anywhere from 5 to 50% of the specifications, but the requirement to test concrete is seldom enforced. As mentioned earlier, testing is required by some design firms and for certain types of structures.

Do you do a calculation on the chloride ion content? Have you included calculated chloride in a submittal? Has calculated chlorides been accepted by the engineer?

Many producers indicated that they do calculate the chlorides and maintain that documentation. In many cases they compare the calculation to measured chlorides. Most producers who do this indicate that the values are considerably less than limits in specifications. Some indicate that they do not submit calculated chlorides. Others indicate that when calculated chlorides are submitted, some engineers accept this, while some design firms will require testing to be performed. Calculated chlorides are often accepted when the project schedule does not permit time for obtaining a test result. Some engineers will conditionally accept calculated chlorides to allow the start of a project but require testing that will govern.

Do you have information on chloride content on materials you use – cementitious, aggregates, admixtures, etc?

Most producers who are impacted by chloride limits in specifications indicate they have information on chemical admixtures and cementitious materials, but not many have this information on aggregates. Some indicate they measure the chloride content of their concrete materials, including mixing water, so that they can calculate the chloride content in concrete.

Have you had chlorides reported on the basis of cementitious materials accepted?

A few producers indicated that they had seen specifications that stated chlorides on the basis of total cementitious materials. Some indicated that concrete mixture submittals reporting chlorides on the basis of cementitious materials have been accepted. As indicated earlier, test reports often state results on different basis.

Many producers responding to the survey are not impacted by chloride limits in specifications and have never had to perform tests on chloride content in concrete. Chloride limits are stated in many specifications but the requirement to test for chlorides is most often not enforced. One commented that some engineers are unsure why it is in their specification or understand its significance. The producers that calculate or test for chlorides indicate that the values they obtain are significantly less than the specification or Code limits. Some mentioned overly conservative limits in some specifications – such as the limit for pre-stressed concrete for reinforced concrete; in one case 0.03%; or the ACI 350 limit of 0.10% for commercial building structures. There were no responses indicating that specifications required the acid-soluble test on concrete or limits in Table 3 as recommended in ACI 222R.

Producers who are impacted by chloride limits suggested that the Code should permit the use of calculated chloride contents and that the limits be revised to be stated on the basis of total cementitious materials.

CONCLUSIONS

Corrosion of reinforcing steel is a significant reason for deterioration of concrete structures. This is primarily impacted by external sources of chlorides that can be addressed by the use of good quality concrete, adequate cover, and the use of corrosion inhibiting admixtures.

Regarding internal chlorides, ACI standards and guides have varying requirements and recommendations on chloride limits for concrete. This can likely cause some confusion to the practicing design professional. Considering the large number of concrete mixtures developed for projects by concrete producers and the potential for different specification requirements on chloride limits, the cost for testing can be significant. However, the specification and enforcement of chloride limits is not extensive and generally limited to some types of structures and by some design firms.

It would be beneficial if internal chloride limits for concrete are based on clearly established threshold concentration levels of chlorides that result in the initiation of corrosion. It is recognized that establishing threshold chloride concentration for wide range of materials and exposure conditions is difficult. Recognizing that calculated chlorides is a conservative estimate of the water-soluble chlorides for the initiation of corrosion, this option should be permitted. The process of measuring the chlorides on concrete materials (test methods) and determining the calculated chloride content should be clearly defined in an ACI document. Lastly, ACI standards should be revised to state chloride limits on the basis of total cementitious materials as most of the concrete mixtures in use include supplementary cementitious materials that are essential for superior performance and durability. It is recognized that these revisions can result in different numerical values for the limits.

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EFFECT OF TEMPERATURE ON THE CHLORIDE BINDING OF PORTLAND CEMENT EXPOSED TO CaCl_2

By Jianqiang Wei, Bernard Tao and W. Jason Weiss

Synopsis: When concrete is exposed to calcium chloride (CaCl_2) deicing salts the concrete may deteriorate or the reinforcing steel may corrode due to the transport of ionic species through its pore structure. As the chloride ions enter the concrete pore structure the ions will either react or be bound by hydration products or will remain free in the pore solution. This work examines the potential reaction that may occur between the CaCl_2 and the calcium hydroxide ($\text{Ca}(\text{OH})_2$) from the paste resulting in the formation of calcium oxychloride. To better understand the role of calcium oxychloride on binding this study investigates the effect of temperature when CaCl_2 solutions are present in Type I and Type V cements at -5, 10, 23 and 40 °C (23, 50, 73.4 and 104 °F). The results indicate that the chloride binding due to calcium oxychloride increases with decreasing temperature. A two part Freundlich isotherm was developed to fit the chloride binding behavior of hydrating cement paste with the first portion considering the common forms of binding (absorption, Friedel's and Kuzel's salts) while the second portion considering binding due to calcium oxychloride formation.

Keywords: binding, calcium oxychloride, chloride, chloride binding isotherm, CaCl_2 , diffusion, Freundlich, ingress, temperature

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INTRODUCTION

It is understood that solutions containing chloride based salts can be transported through the pore structure of concrete. Numerous publications describe this transport. The chloride ions can either move freely in the pore space or may be bound as a part of the hydrated cement. While the vast majority of reported studies focus on chloride binding isotherms obtained at room temperature; temperature can influence the chloride binding capacity of the hydrated cement paste.

Some studies have investigated the influence of temperature on chloride binding. Roberts¹ reported that the amount of bound chloride decreased with elevated temperature. Dousti and Shekarchi² observed that the highest binding capacity was observed at room temperature in studying samples between -4 °C and 70 °C (23 to 104 °F). Panesar and Chidiac³ obtained a greater chloride binding for cold temperature which they reported as due to the decreased thermal vibration of chloride ions and the formation of ice in the chloride solution. Hussain⁴ and Maslehuddin^{5, 6} reported a reduction of chloride binding in cement as temperature increased and this is in agreement with the results reported by Larsson⁷. This increased binding was attributed to the decreased solubility of Friedel's salt and calcium chloro-aluminate phase, which results in more free chlorides at equilibrium^{1, 8}. Zibara⁹ found that a decreased temperature caused a greater chloride binding at low chloride concentration; while a reverse was observed at high chloride concentration (3.0 M). Enhanced chloride binding was observed by Yuan¹⁰ as temperature increases from 5 to 40 °C (41 to 104 °F) in the presence of NaCl. It can be noticed that although the trends in reports are not consistent, most of the results indicate a decreased chloride binding of cement at an elevated ambient temperature and there appears to be a dependence on the concentration of the chloride as well. More importantly, except Roberts¹, all the results were obtained based on sodium chloride (NaCl) and salts like calcium chloride (CaCl₂) and magnesium chloride (MgCl₂) have been studied much less frequently.

It is well known that chloride ions can react with both unhydrated and hydrated aluminate phases to form Friedel's salt and Kuzel's salt¹¹⁻¹³. However, a recent investigation shows that a calcium oxychloride (3CaO·CaCl₂·15H₂O) phase can be formed through the reaction between calcium chloride (CaCl₂) and calcium hydroxide (Ca(OH)₂) in the cementitious matrix^{14, 15} for a higher concentration of CaCl₂ and/or MgCl₂. Monosi and Collepardi¹⁶ reported the presence of oxychloride identified by X-ray diffraction of the wet hardened cement paste samples that have been immersed in 30 wt.% CaCl₂ solution under 5 °C (41 °F) for 2 months. In addition, they also found that this paste disappeared if the samples were ground, washed with methyl alcohol and dried at a low relative humidity (≤1%). This formation and unstable nature of oxychloride was observed by Shi¹⁷, Birnin-Yauri and Glasser¹⁸ based on X-ray diffraction analysis. Petrographic evidence of oxychloride formation was presented by Sutter et al¹⁹ based on optical microscopy, scanning electron microscopy and microanalysis. They reported that these oxychloride phases form through consumption of portlandite and precipitation in voids in cracks, where calcium oxychloride pseudomorphs can be observed after portlandite crystals. Recently, the rate of formation for calcium oxychloride in cement in the presence of CaCl₂ deicing salt was determined by Farnam and Weiss¹⁵ using Low Temperature Differential Scanning Calorimetry and Isothermal Micro-Calorimetry. Equation (1) describes the reaction that can result between CaCl₂ and Ca(OH)₂ to form calcium oxychloride:

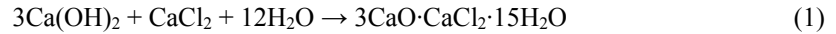


Figure 1 illustrates a phase isopleth that describes the temperature concentration dependence that is exhibited when CaCl_2 is added to a solution containing calcium hydroxide ($\text{Ca}(\text{OH})_2$) (like that exhibited in a cement paste system) to form calcium-oxychloride.

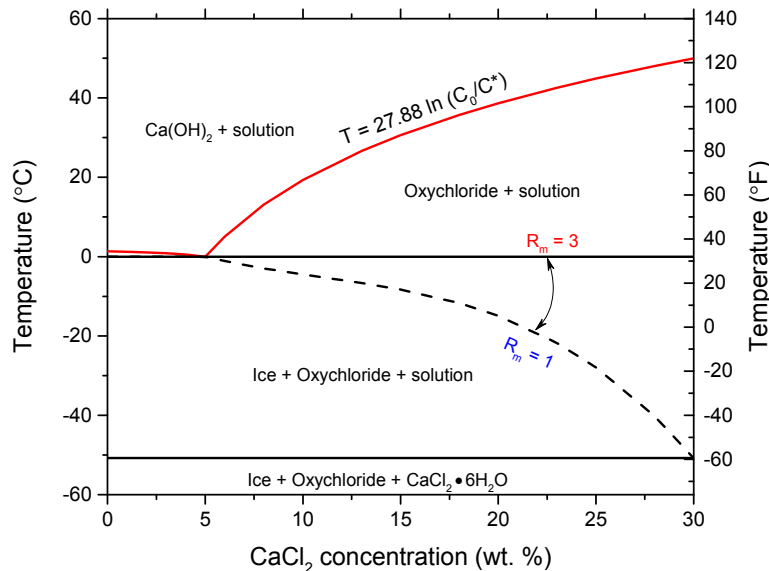


Figure 1 — Phase diagram for $\text{Ca}(\text{OH})_2$ - CaCl_2 - H_2O system^{15, 20} ($R_m = \text{Ca}(\text{OH})_2/\text{CaCl}_2$ molar ratios)

Figure 1 describes the behavior of the ternary $\text{Ca}(\text{OH})_2$ - CaCl_2 - H_2O system. Farnam and Weiss¹⁵ approximated the phase boundary at which calcium oxychloride forms as Equation (2):

$$T = 27.88 \ln (C_0 / C^*) \quad (2)$$

where T (°C) is sample temperature, C_0 is the initial CaCl_2 concentration associated with the formation of calcium oxychloride, and C^* (=4.97 wt. %) is the intersection between $\text{Ca}(\text{OH})_2$ and calcium oxychloride phase boundary (the liquidus line) and the phase boundary for ice formation, so it demonstrates the theoretical minimum CaCl_2 concentration solution at which the calcium oxychloride forms. From this model, it can be seen that the formation of calcium-oxychloride and the corresponding chloride binding should have a strong temperature dependence.

In addition to being influenced by temperature, carbonation is another factor that should be taken into consideration for chloride binding. By exposing a cementitious matrix to gaseous CO_2 , the calcium hydroxide and calcium silicate hydrates (C-S-H) may carbonate, however the calcium hydroxide will preferably react especially at low concentration. The carbonation process can be described as a chemical reaction of calcium hydroxide with carbon dioxide resulting in the formation of calcium carbonate and water²¹ as follow:



Kayyafi et al.^{22, 23} investigated accelerated carbonation on chloride binding of cement paste and observed a decrease in chloride binding capacity. Zibara⁹ investigated the effect of carbonation on chloride binding capacity of cement paste in the presence of external sodium chloride. The reduction of calcium hydroxide through accelerated carbonation has been proven as an effective way to mitigate the formation of calcium oxychloride^{24, 25}.

RESEARCH SIGNIFICANCE

Chloride binding plays an important role in the transport of chloride ions in concrete. While binding has been studied for many decades, this paper suggests that the potential reaction between the hydrated cement matrix and CaCl_2 deicing salt solutions may require further study. Specifically, the $\text{CaCl}_2\text{-H}_2\text{O-Ca(OH)}_2$ phase isopleth suggests the formation of calcium oxychloride at high CaCl_2 concentration which can substantially influence the chloride binding. This work examines the effect of temperature on chloride binding capacity of hydrated portland cement paste in the presence of CaCl_2 deicer. Two types of cement (type I and V) and four temperatures, -5°C , 10°C , 23°C and 40°C (23 , 50 , 73.4 and 104°F), were used. The influence of carbonation was also studied. An equation was developed to describe chloride-binding isotherms that accounts for calcium oxychloride.

EXPERIMENTAL PROCEDURE

Materials used in making cement pastes

Type I and Type V ordinary portland cements were used in this study with a reported Blaine fineness of $375\text{ m}^2/\text{kg}$ ($1830\text{ ft}^2/\text{lb}$) and $316\text{ m}^2/\text{kg}$ ($1542\text{ ft}^2/\text{lb}$), respectively. The chemical compositions of the two types of cement are summarized in Table 1. Type V cement contains less C_3A than Type I. As a result, it would be expected to form less Friedel and Kuzel salt (however this may also be impacted by the increase in C_4AF).

Table 1 — Chemical and mineralogical composition of Type I and Type V cements.

Chemical and phase composition					
Chemical composition in equivalent oxide [wt. %]			Phase composition of cement [wt. %]		
Oxide	Type I	Type V		Type I	Type V
CaO	63.5	63.2	$\text{C}_3\text{S}^{\text{a}}$	60	64
SiO_2	19.4	21.3	$\text{C}_2\text{S}^{\text{b}}$	10	13
Fe_2O_3	3.18	4.20	$\text{C}_3\text{A}^{\text{c}}$	9	0
Al_2O_3	5.39	2.60	$\text{C}_4\text{AF}^{\text{d}}$	10	13
SO_3	3.38	2.80	Readily soluble equivalent alkalis as Na_2O [wt%]		
MgO	2.97	4.50			
K ₂ O	0.77	-			
Na_2O	0.35	-			
Free lime	-	0.38			
Loss on ignition	0.88	1.20		0.86	0.21
Insoluble residue	0.25	0.18			

^a Tricalcium silicate; ^b Dicalcium silicate; ^c Tricalcium aluminate; ^d Tetra-calcium Aluminoferrite

Preparation of specimens

A water to cement ratio (w/c) of 0.42 was used throughout this study. The cement pastes were mixed following a procedure similar to ASTM C305-14; however a vacuum mixer was used a speed of 400 rpm^{15, 26}. After mixing, samples were cast in 76.2 cm (diameter) x 152.4 cm (height) (3 x 6 in) cylindrical molds. The samples were sealed and cured at $23\pm 2^\circ\text{C}$ for over 3 months. The well hydrated cement pastes were then ground layer by layer from the middle in 2 mm (0.079 in) lifts using a milling machine³⁰. The cement powder was then collected and passed through a 45 μm (0.0018 in) sieve.

Materials used in making CaCl_2 solutions

Granular reagent calcium chloride dehydrate was used. De-ionized (DI) water was used as the solvent.

Accelerated carbonation

A carbon dioxide (CO_2) chamber was employed to accelerate the carbonation process at room temperature. A relative humidity of 55% was used.^{22, 27, 28} The relative humidity was maintained using saturated sodium bromide solution. A CO_2 concentration of 1.5% was used. In order to fully carbonate the hydrated cement, powders were placed in the CO_2 chambers for 10 days until the mass of samples reach equilibrium. This was shown to result in nearly complete calcium hydroxide consumption (and/or encapsulation).²²

Equilibrium method for chloride binding

Before mixing with the CaCl_2 solutions, both the plain and carbonated cement samples were conditioned to a temperature of $23 \pm 1^\circ\text{C}$ ($73.4 \pm 1.8^\circ\text{F}$) and a relative humidity of 11% for 2 weeks in a sealed desiccator containing saturated lithium chloride solution. Following the procedure developed by Tang and Nilsson²⁸, after the mass of samples reached equilibrium, both the cement powder and solutions were separately sealed using plastic bottles and conditioned at the four temperatures for three days. Then 4 g of cement powder was uniformly mixed and immersed in 10 ml CaCl_2 solutions with different concentrations as shown in Figure 2. This cement powder to solution ratio was selected according to the recommendation reported by Delagrave et al²⁹, who mixed approximately 20 g powder with 50 ml solution in their study. Thirteen CaCl_2 solutions were prepared at different CaCl_2 concentrations (0.5, 1.5, 2.5, 3.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, and 30 wt. %) for all the four temperatures.

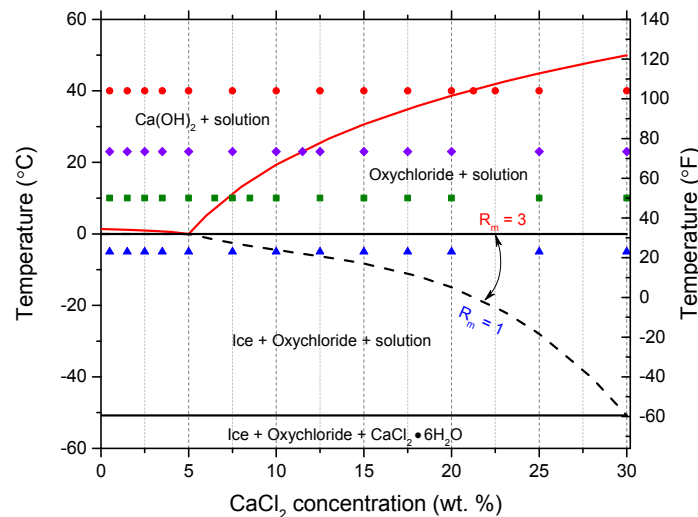


Figure 2 — CaCl_2 solution design for chloride binding under different temperatures

The critical chloride concentration for the formation of calcium oxychloride is a function of temperature. Equation 2 can be rearranged to calculate this concentration as shown in equation 4:

$$C_{I-Oxy} \% = \exp\left(\frac{T+44.68}{27.88}\right) \quad (4)$$

where $C_{I-Oxy} \%$ is the critical chloride concentration at which calcium oxychloride begins to form and T is the temperature in $^\circ\text{C}$. This equation describes the development of phase boundary between Ca(OH)_2 and calcium oxychloride (the red liquidus line in Figure 2) in a calcium chloride range from 5 wt. % to 35 wt. %.

According to Eq. (4), additional CaCl_2 solutions with concentrations in close proximity to the phase boundary were prepared as shown in Figure 2, such as 6.5 wt. % and 8.5 wt. % for 10°C (50°F), 21.25 wt. % and 22.5 wt. % for 40°C (104°F), and 11.5 wt. % for 23°C (73.4°F).

The chloride binding samples (cement powder + solutions) were placed in vials, which were sealed to minimize the potential for the evaporation of water. The vials were placed in four chambers with temperatures of $-5 \pm 1^\circ\text{C}$, $10 \pm 1^\circ\text{C}$, $23 \pm 1^\circ\text{C}$, and $40 \pm 1^\circ\text{C}$ (23 , 50 , 73.4 and 104°F) for 2 months to ensure that it is sufficient to reach the equilibrium between the solid and the solution. This time was confirmed by performing additional measurements on selected samples at all the four temperatures. After the reaction between the solutions and powders reached steady state, the exact chloride concentrations of the initial solutions and the equilibrium free chloride concentrations of the extracted solutions were determined by using an automated titration unit through potentiometric titrations with a 0.0102 M AgNO_3 electrode. The silver nitrate was added in 0.2 ml increments (this addition rate however decreases while approaching the saturation point), while simultaneously the electric potential of the solution was monitored with a silver reference electrode. The chloride content of the solution is determined using the dosage of silver nitrate

once the maxima of the first derivative curve of the potential reached³⁰. The amount of bound chlorides (C_b) (mg / g sample, 0.001 lb / lb sample) was then calculated by using equation 5³¹:

$$C_b = \frac{35.45 (C_0 - C_1) V}{W} \quad (5)$$

where V is the volume of CaCl_2 solution (10 ml) (0.34 fl oz), C_0 is the initial concentration of chloride solution (mol / L, 0.0296 mol / fl oz), C_1 is the equilibrium concentration of CaCl_2 solution (mol / L, 0.0296 mol / fl oz), and W is the mass of cement powder (4 g) (0.0088 lb).

RESULTS AND DISCUSSION

Effect of temperature on chloride binding

Figure 3 shows the chloride binding isotherms of Type I and Type V hydrated cement paste in the presence of CaCl_2 solutions at -5, 10, 23 and 40 °C (23, 50, 73.4 and 104 °F). Each data point represents the average of two measurements and the corresponding coefficients of variation are less than 6.0%. It can be seen that for both the Type I and Type V cement pastes, the amount of bound chloride increases significantly with increased free chloride at low concentrations (≤ 5 wt. %) regardless of temperature. This has been conventionally attributed to physical chloride binding by the cement hydration products, such as C-S-H, C-A-H, C-A-S-H and ettringite, and chemical binding between chloride ions and monosulfate and aluminate phases. Due to the lower C_3A content in the samples made using Type V cement, less chloride was bound in the Type V cement paste than that bound in the Type I cement paste under each temperature. Although the chloride binding behavior of cements may show a slight temperature dependence at low concentrations, this temperature dependence is relatively small compared with that at high CaCl_2 concentrations (and the influence of temperature at low concentrations is not considered in this study).

An inflection point was observed in the chloride binding isotherms for both the Type I and Type V hydrated cement pastes at each temperature. The inflection points are located approximately at CaCl_2 concentrations of 5 wt. %, 7.5 wt. %, 11.5 wt. % and 20 wt. %, for -5, 10, 23 and 40 °C (23, 50, 73.4 and 104 °F), respectively. Beyond these inflection points, the amount of bound chloride increases more substantially. According to the liquidous line showing the boundary of phase formation in Figures 1 and 2, this inflection point is attributed to the formation of calcium oxychloride, which binds chloride ions. From Figure 3, it can be seen that as the temperature that the sample was stored at was decreased, the CaCl_2 concentration at which the inflection point occurred decreased and more chloride was bound.

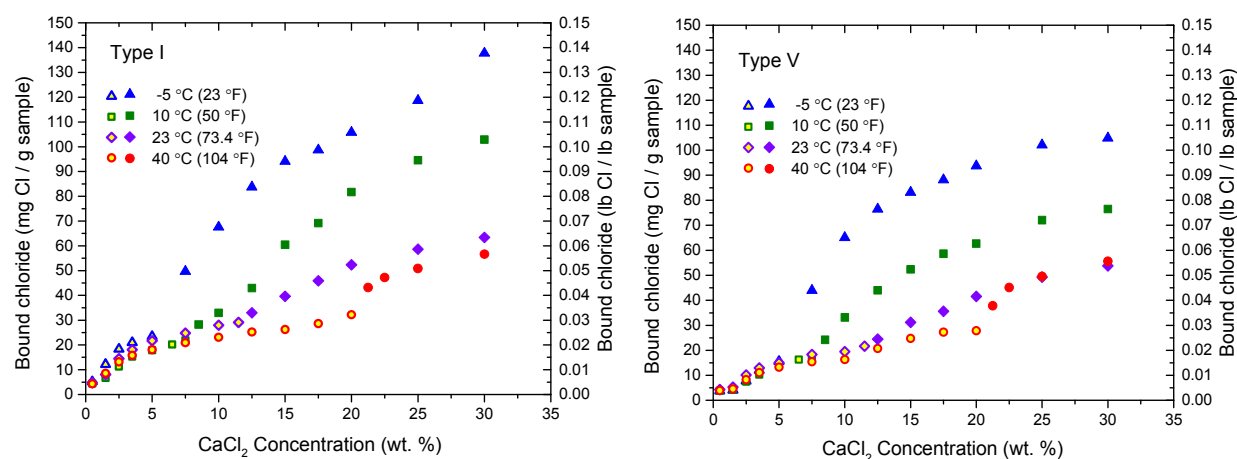


Figure 3 — Chloride binding isotherms of Type I and Type V cement under different temperatures.

Chloride-binding isotherms for low CaCl₂ concentrations

Figure 4 shows the chloride binding isotherms for Type I and V cement paste at -5 and 40 °C (23 and 104 °F) using a single curve which is typical of the approach commonly used by many currently. (Note a single Freundlich curve is commonly used to describe the entire range of CaCl₂ concentrations). It can be seen that, simply fitting the data by using a single isotherm may fail to capture specific features of the curve. For example, the single isotherm does not appear to fit the data well at lower CaCl₂ concentrations (e.g., 3 to 10% for the 5 °C sample and from 3 to 20% for the 40 °C sample).

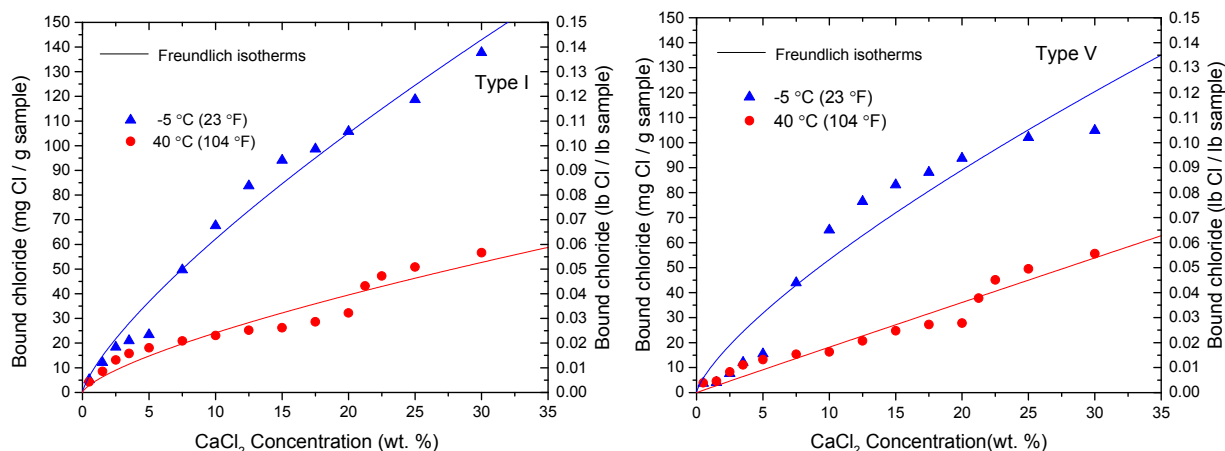


Figure 4 — Oversimple Freundlich isotherms for Type I and V cement under -5 and 40 °C.

Several mathematical models have been employed in the literature to fit the chloride-binding isotherms, such as linear isotherm³², Langmuir non-linear isotherm³³, Freundlich isotherms²⁹, and the combination of Langmuir (low concentrations) and Freundlich (high concentrations) isotherms³¹. Equation (6) (the Freundlich isotherm) was used in this study due to its ability to best reflect the trends in data. Equation (6) describes the chloride binding:

$$C_b = \alpha C_f^\beta \quad (6)$$

where α and β are constants, C_f is the initial free chloride concentration (wt %), and C_b is bound chloride (mg chloride / g sample).

The relationship between the bound chloride (C_b) and free chloride (C_f) for concentrations lower than that associated with the than inflection points for all the four temperatures was fitted by using a single isotherm which was assumed to be independent of temperature (note strictly speaking a temperature dependence likely exists however a single curve appeared to fit the data reasonably well). Figure 5 shows the isotherms obtained by using the Freundlich fitting curves. The isotherm regression parameters for each isotherm are summarized in Table 2. The Freundlich isotherms fit the data well for Type I and Type V, respectively.

Chloride-binding isotherms of cement in the presence of CaCl₂

When the concentration of CaCl₂ increases to a concentration greater than the inflection point that is associated with the formation of calcium hydroxide a considerable increase in the amount of bound chloride can occur. In order to fit the chloride binding to the data more accurately a two-part Freundlich curve was used. At low concentration a term like that shown in Equation (6) was used to account for the bound chloride physical binding and the formation of Friedel's and Kuzel's salts. At higher concentration the bound chloride, due to the formation of calcium oxychloride, was also taken into account. A two-part Freundlich isotherm is described in Equation (7a and 7b):

$$C_b = \alpha C_f^\beta \quad \text{when } C_f \leq C_{I-ox} \quad (7a)$$

$$C_b = \alpha C_f^\beta + \alpha_{oxy} (C_f - C_{I-ox})^{\beta_{oxy}} \quad \text{when } C_f > C_{I-ox} \quad (7b)$$

where C_b is the total amount of bound chloride, α and β (as shown in Table 2) are the regression parameters for low CaCl_2 concentration, and α_{oxy} and β_{oxy} describe the chloride binding due to calcium oxychloride formation. Using Eq. (4), the concentrations of CaCl_2 (C_{I-Oxy}) associated with the formation of calcium oxychloride could be calculated for the four temperatures and these results are summarized in Table 3. Figure 6 shows the chloride binding isotherms of Type I and Type V cement for the four temperatures fitted by the two-part Freundlich curves. Using the regression parameters shown in Table 3, it can be seen that the two part Freundlich isotherms fit the data well.

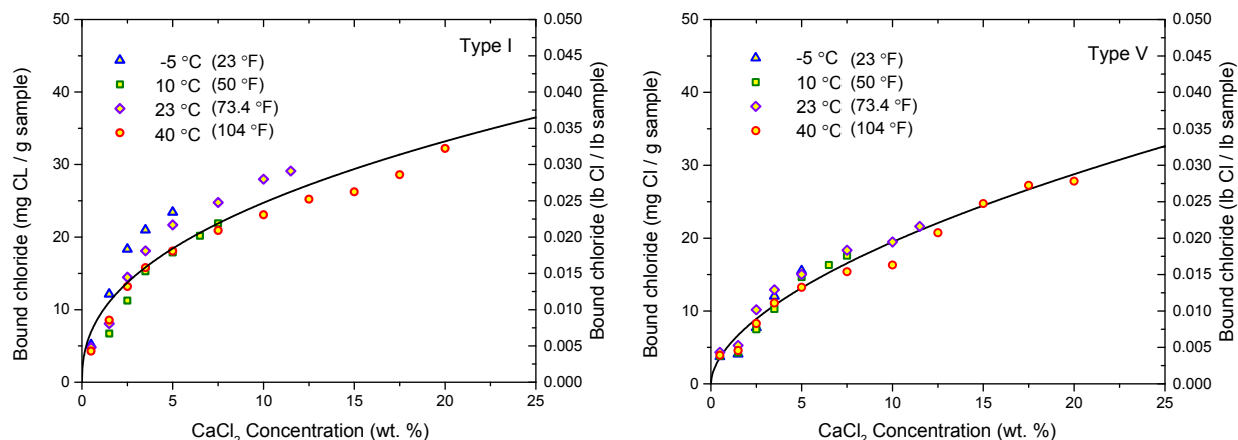


Figure 5 — Mathematical models to fit chloride binding isotherms of Type I and V cements for low concentrations that no calcium oxychloride forms.

Table 2 — Freundlich isotherm regression parameters for Type I and V cements at low salt concentrations.

Cement	α	β	R^2
Type I	9.30	0.42	0.89
Type V	5.32	0.56	0.96

Table 3 — Parameters of the Freundlich isotherm for chloride binding of Type I and Type V cement due to calcium oxychloride formation.

Cement	Temperature (°C)	C_{I-Oxy} (wt. %)	Freundlich		
			α_{Oxy}	β_{Oxy}	R_2
Type I	-5 (23 °F)	4.15	16.75	0.54	0.98
	10 (50 °F)	7.11	5.27	0.82	0.97
	23 (73.4 °F)	11.33	5.91	0.49	0.99
	40 (104 °F)	20.85	10.96	0.20	0.99
Type V	-5 (23 °F)	4.15	23.78	0.35	0.94
	10 (50 °F)	7.11	8.99	0.51	0.98
	23 (73.4 °F)	11.33	3.03	0.62	0.99
	40 (104 °F)	20.85	11.56	0.25	0.97

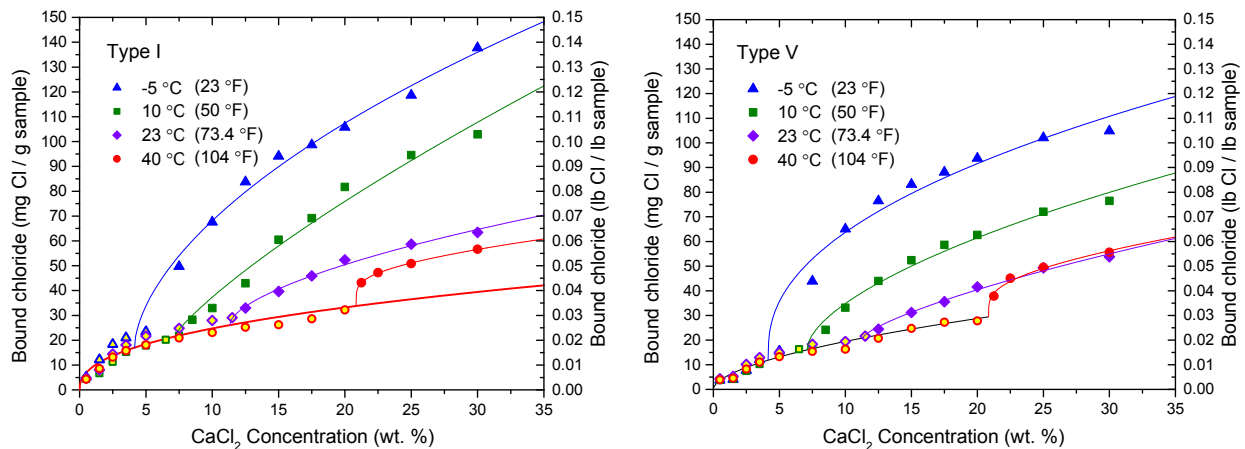


Figure 6 — Chloride binding isotherms for Type I and Type V cement by using piecewise Freundlich isotherms.

Contribution of calcium oxychloride

A substantial increase in the chloride binding capacity of the hydrated cement paste at high CaCl_2 concentrations is attributed to the formation of calcium oxychloride. In this study, as shown in Figure 7, the amount of bound chloride due to the formation of calcium oxychloride under each temperature was simply determined using the second part of equation (7), which indicates the differences between Freundlich isotherms at high CaCl_2 concentrations and the extending line of the Freundlich isotherm at low concentrations.

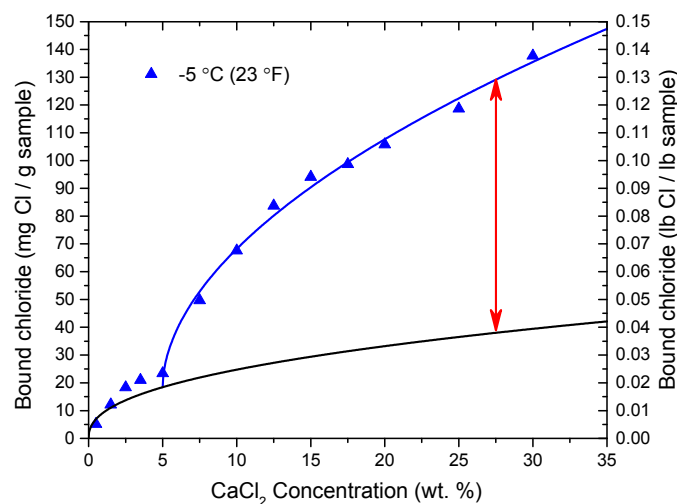


Figure 7 — Difference between isotherms due to formation of calcium oxychloride.

Figure 8 shows only the contribution of the binding curve associated with calcium oxychloride formation (i.e., the second portion of Equation (7b)). It can be seen that, the amount of calcium oxychloride decreases with an increasing temperature, and consequently less chloride was bound. It can be noticed (when comparing Figures 8a and 8b) that less chloride was bound by Type V cement than Type I cement at high CaCl_2 concentrations. This can be attributed to a reduction in the formation of calcium hydroxide in Type V cement pastes which results in less calcium oxychloride formation.

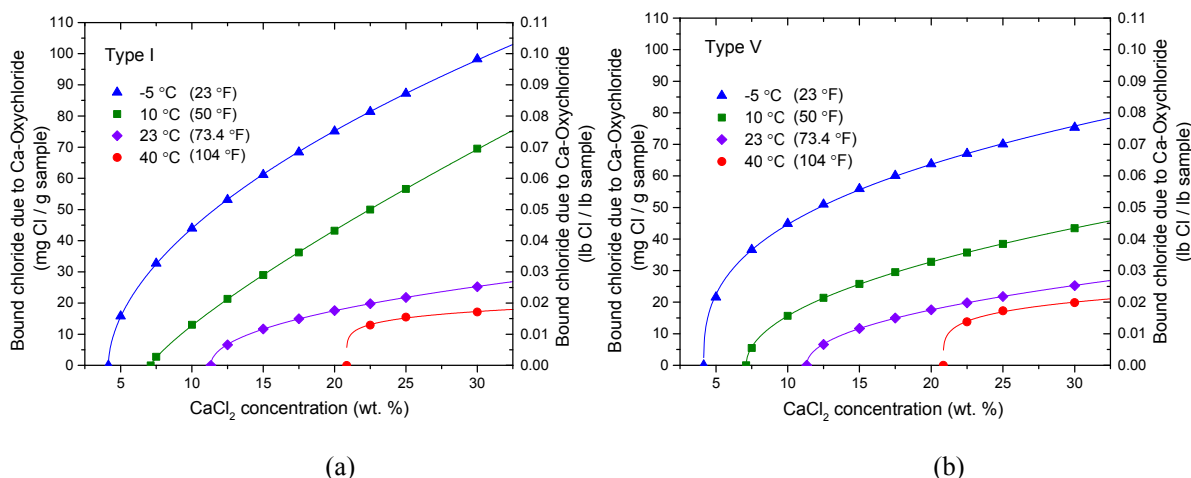


Figure 8 — Bound chloride due to the formation of calcium oxychloride for Type I (a) and Type V (b) cement.

Influence of carbonation on chloride binding

Figure 9 shows the chloride binding behavior of hydrated pastes made using Type I and Type V cements before and after carbonation. The carbonation of the hydrated cement paste reduces the amount of accessible calcium hydroxide^{9, 24}. As a result, carbonation can reduce the chloride binding capacity at both low and high CaCl_2 concentrations resulting in less Friedel's salt formation and less calcium oxychloride formation. From Figure 10, it can be seen that at 23°C (73.4°F) the amount of chloride binding decreases. In addition, Figure 10 shows that the inflection point on the chloride binding isotherm associated with calcium oxychloride formation disappears. This reduction in calcium oxychloride is likely attributed to the inability to form calcium oxychloride due to the removal (or encapsulation) of calcium hydroxide after carbonation²⁵.

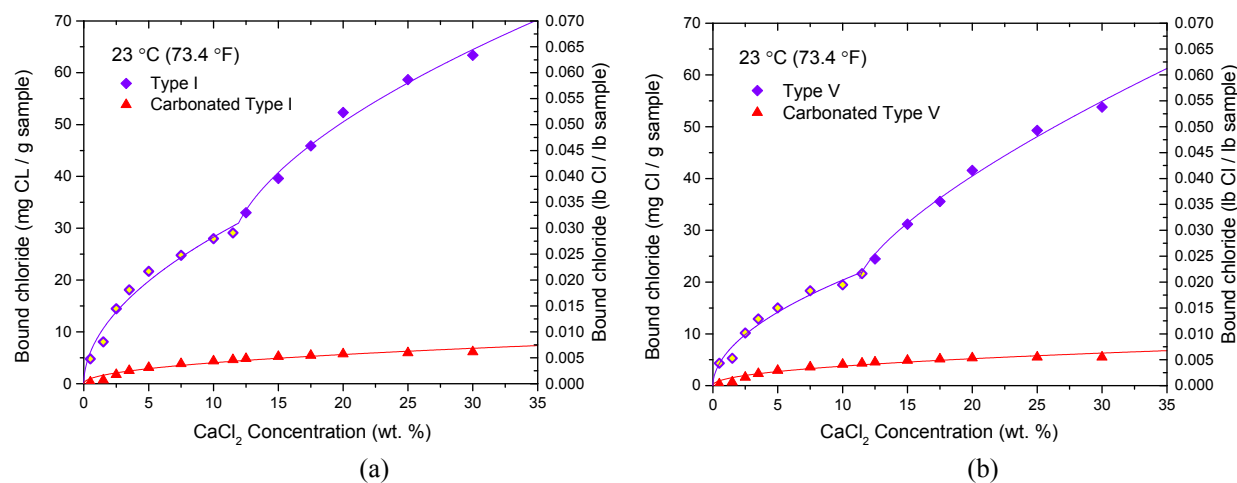


Figure 9 — Chloride binding behavior of Type I (a) and Type V (b) cement with and without carbonation.

CONCLUSIONS

This paper examined the influence of temperature on the chloride binding behavior of hydrated cement pastes made using Type I and Type V cement. Specifically, this work examined the binding that occurs between the ionic species in CaCl_2 salt solutions and the hydrated cement paste at varying temperatures. The results indicate that the chloride binding capacity at high CaCl_2 concentrations decreases with the increasing temperature. This temperature

dependency is proposed to be due to the formation of calcium oxychloride which occurs specifically at high CaCl_2 concentrations. It was shown that the concentration at which calcium oxychloride forms was likely to be changed with sample/solution temperature which was consistent with the phase isopleth for the $\text{CaCl}_2\text{-H}_2\text{O-Ca(OH)}_2$ system. The formation of calcium oxychloride resulted in an inflection point (that was linked to the liquidus curve on the phase isopleth) in the chloride binding isotherm. This demonstrates that more chloride ions were bound by the hydrating cement paste, and the amount of free chloride in the pore solutions decrease. As a result a two part Freundlich isotherm was developed to fit the chloride binding behavior of both Type I and Type V cements at both low and high salt concentrations. As expected the carbonation of the cement paste resulted in significant reductions in their chloride binding capacity. Carbonation resulted in a significant reduction (or encapsulation) of calcium hydroxide, which is responsible for chloride binding (through the formation of calcium oxychloride) at high CaCl_2 concentrations.

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PROBABILISTIC TREATMENT OF CHLORIDE THRESHOLD

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Synopsis: Chloride threshold is known to be a variable value depending on many parameters related to the cement chemistry, concrete characteristics and external environment. Several studies have been performed trying to find a general law that can predict the threshold in a particular concrete. Although this goal is the most rigorous approach to solving the problem, it seems very difficult to measure all influencing parameters in real work. Another approach consists in analysing the variability in a rational way. This is done in the present work following a recent method suggested in the new Model Code 2010, which considers deterministic to probabilistic models for service life prediction. The depassivation event is analysed first from its progressive nature which aims to determine chloride threshold variability, whose statistical distribution has been measured in the laboratory and which has shown to agree with observations in real structures. Also, comments are given on the meaning of the probability of depassivation and its consideration from a structural point of view. Finally an accelerated test method is mentioned which enables the determination of the chloride threshold in testing times shorter than 4 to 8 weeks. Testing of samples containing portland cement only and portland cement with slag are assessed with the accelerated test.

Keywords: Chloride; Concrete; Corrosion; Statistics; Testing; Threshold.