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CALCIUM CHLORIDE IN CONCRETE $\frac{1}{2}$ APPLICATIONS AND AMBIGUITIES

by V. S. Ramachandran

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Calcium chloride in concrete — applications and ambiguities¹

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Many aspects of the action of calcium chloride in concrete are ambiguous, controversial, or incompletely understood. Examples include: (a) the restrictive definition of calcium chloride as an accelerator; (b) the lack of clarity in prescribing the dosage for practical applications; (c) the classification of calcium chloride as an antifreezing agent; (d) the misconception regarding corrosion of reinforcement in the presence of CaCl_2 ; (e) the divergence of opinion on the mechanism of action; and (f) incomplete understanding of the changes in the intrinsic properties of cement containing calcium chloride. This paper attempts to deal with these aspects citing typical examples.

Plusieurs aspects de l'action du chlorure de calcium dans le béton sont ambigus, controversés ou incomplètement compris. On peut citer entre autres: (a) la définition limitative du chlorure de calcium en tant qu'accélérateur; (b) le peu de clarté dans la définition du dosage pour des applications pratiques; (c) la classification du chlorure de calcium en tant qu'agent antigel; (d) les conceptions erronées touchant la corrosion des armatures en présence de CaCl_2 ; (e) les divergences d'opinion sur le mécanisme de l'action du CaCl_2 ; et (f) la compréhension incomplète des changements intervenant dans les propriétés intrinsèques du ciment contenant du chlorure de calcium. Cet article étudie ces aspects du problème dont il fournit des exemples types.

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Concrete, made with cement, water, and aggregates comprises in quantity the largest of all man-made materials. Concrete is a composite material in which the binding matrix is the cement paste formed by the reaction of the Portland cement with water; the filler material is the aggregate. The aggregates (coarse and fine) may comprise about three quarters of the volume of concrete; the air voids, together with cement paste, occupy the rest. As the active constituent in concrete is the cement paste, the performance of concrete is determined, to a large extent, by the type and amount of cement paste contained in it. Many concretes are made with small amounts of materials called 'admixtures', which may influence the physical, chemical, and mechanical properties of the cement paste and hence of the concrete.

The addition of small amounts of certain materials to concrete to promote desirable properties is as old as the use of cement itself. The Romans used blood, pig's fat, and milk as additions to pozzolanic cements to improve their workability and durability. Today, many hundreds of chemicals, claimed to possess one or more beneficial effects, have been advocated for incorporation in concrete. Typical examples of admixtures include water reducers, retarders, water reducing-accelerating agents, waterproofer, air-entraining agents, and accelerators.

Addition of an accelerator increases the rate of setting and strength development in concrete. Many

substances are known to act as accelerators for concrete, including calcium formate, aluminum chloride, potassium carbonate, sodium chloride, and calcium chloride. Of these, calcium chloride is the most widely used because of its ready availability, low cost, predictable performance characteristics, and successful application over several decades. Calcium chloride is also an important component of many multi-component admixture formulations and is also a constituent of de-icing salt. In the Soviet Union, large additions of calcium and sodium chloride (22.5% by weight of water) have been advocated for lowering the freezing point of water added to concrete (Mironov *et al.* 1968).

Calcium chloride has been used as an admixture longer than most other admixtures. The first documented use of calcium chloride in concrete can be traced to the year 1873 (Kuhl and Ullrich 1925) and the first patent to the year 1885 (Millar and Nichols 1885). Prior to 1900, there were only about seven publications concerning the use of calcium chloride in Portland cement, but since then the literature has grown substantially. The interest in this admixture is evident from innumerable papers, patents, reviews, chapters in books, and symposia; a book has been published recently discussing the science and technology concerning the use of calcium chloride in concrete (Ramachandran 1976).

Action of Calcium Chloride

Concrete has to satisfy many performance requirements. The addition of calcium chloride promotes

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TABLE 1. Some of the properties influenced by the use of calcium chloride admixture in concrete

Property	General effect	Remarks
Setting	Reduces both initial and final setting	ASTM standard requires that the initial and final setting time should occur at least 1 h earlier with respect to the reference concrete
Compressive strength	Increases significantly the compressive strength in the first three days of curing (gain may be about 30–100%)	ASTM requires an increase of at least 125% over the control concrete at 3 days. At 6–12 months, the requirement is only 90% of the control specimen
Tensile strength	A slight decrease at 28 days	This figure may vary depending on the starting materials and method of curing. The decrease may be more at 28 days
Flexural strength	A decrease of about 10% at 7 days	
Heat of hydration	An increase of about 30% in 24 h	The total amount of heat at longer times is almost the same as that evolved by the reference concrete
Resistance to sulfate attack	Reduced	This can be overcome by the use of Type V cement with adequate air entrainment
Alkali–aggregate reaction	Aggravated	Can be controlled by the use of low alkali cement or pozzolana
Corrosion	Causes no problems in normal reinforced concrete, if adequate precautions taken. Dosage should be kept below 1.5% CaCl_2 and adequate cover given. Should not be used in concrete containing a combination of dissimilar metals or where there is a possibility of stray currents	Calcium chloride admixture should not be used in prestressed concrete or in a concrete containing a combination of dissimilar metals
Shrinkage and creep	Increased	At later ages may be less resistant to frost attack
Volume change	Increase of 0–15% reported	
Resistance to damage by freezing and thawing	Early resistance improved	
Watertightness	Improved at early ages	At longer periods almost same with respect to reference concrete
Modulus of elasticity	Increased at early ages	
Bleeding	Reduced	

certain desirable properties and affects others (Table 1).

The most important use of calcium chloride as an admixture in concrete is related to its ability in reducing the initial and final setting times of concrete and accelerating the hardening of concrete. From the practical point of view, this means reduction in the curing period and reduction in the time during which concrete must be protected in cold weather, earlier finishing operations, and earlier availability for use. The influence of different amounts of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

on the initial and final setting times of a neat cement paste is indicated in Fig. 1 (Ramachandran 1974a). As can be seen in the figure, as the amount of added calcium chloride is increased, the setting periods are reduced. Excessive amounts (for example, 4%) cause a very rapid set, however, and are avoided.

Figure 2 refers to the strength development in concretes made with 2% CaCl_2 and cured up to 28 days at a temperature of 70°F (21.1°C) (Shideler 1952). All concretes show considerable strength gain at early ages. It is also obvious that it takes only $1\frac{1}{2}$

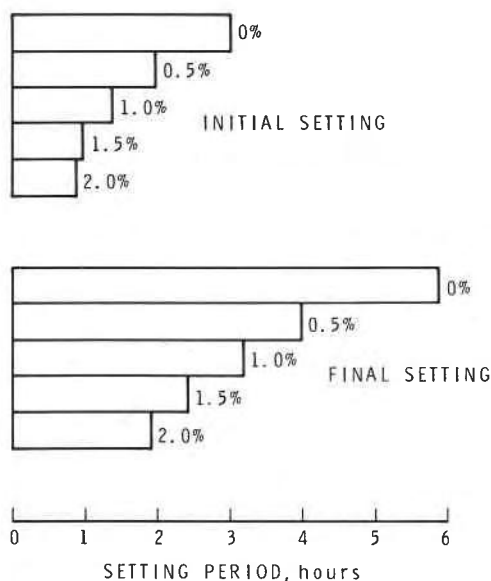


FIG. 1. Initial and final setting periods of a cement paste containing different amounts of calcium chloride (Ramachandran 1974a).

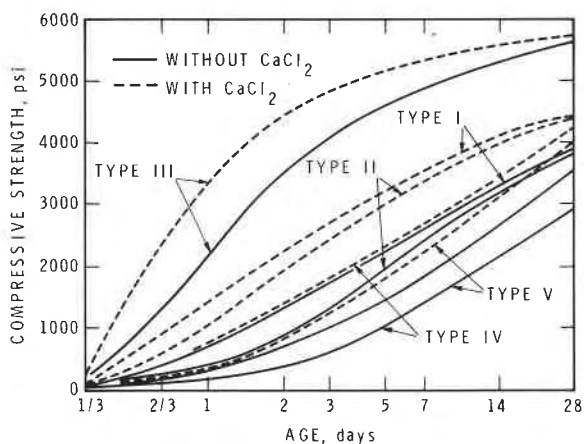


FIG. 2. Influence of calcium chloride on strength development in concretes made with different types of cement (Shideler 1952).

days for concretes with CaCl_2 to develop a strength that can only be attained at about 3–3½ days with the reference concrete containing no CaCl_2 . Although it is obvious that there is an early strength gain in concrete with CaCl_2 , it is not easy to predict in quantitative terms. Even maintenance of the same cement content, amount of CaCl_2 , air and slump does not ensure a similar influence of CaCl_2 on strength characteristics. For example, concretes with 13 cements obtained from different sources were cured for 7–28 days in the presence of CaCl_2 . Calcium chloride caused slight to moderate increases in the 7-day compressive strengths of 11 out of 13 cements.

At 28 days the compressive strengths of 9 out of 13 cements containing CaCl_2 were less than the compressive strengths of their corresponding reference mixes (Roskopf *et al.* 1975).

The performance of a concrete containing calcium chloride can be predicted reasonably only when both the short- and long-range effects have been established. Such knowledge permits judicious use of admixtures. Originally, the science of admixture was the province of a specialist. With advanced building technology, however, and ever-increasing new demands on builder, engineer, and architect it is necessary that all involved in building have some knowledge of admixtures and their effects on cement, aggregate, or the mixing water.

Compared with many other complex admixtures, calcium chloride is relatively simple in terms of its chemical and physical nature. It would seem, therefore, that its action on cement hydration would be easy to understand. An assessment of the research of the last several decades has revealed that there is little justification for this presumption. Not only is there much controversy regarding the actual mechanism of the action of calcium chloride, but there is persistent misunderstanding and disagreement on its effects on and use in concrete. In the following, an attempt will be made to discuss some of these aspects from the standpoint of an applied chemist; the use of complex chemical equations has deliberately been excluded.

Accelerating Action – Implications

In cement science, as in other branches of study, certain terms are so commonly used that they are accepted without reservation. Lack of appreciation of the limitations and assumptions implicit in their definition may lead to misinterpretation or even confusion, both from the viewpoint of research and practical application of admixtures in concrete. One of the statements made by Le Chatelier (1919) at the First International Symposium on the Chemistry of Cements is relevant even today. He stated, "People evade defining what they call a colloid, but they seem to take the word in the sense of a body capable of hardening. And then the explanation comes down to this. Cements harden because they have the property of hardening ..."

The definition in concrete technology of a chemical accelerator is generally taken from standard specifications. The definition, however, is not the same in different standards. The American Society for Testing and Materials (1977) defines an accelerator as "an admixture that accelerates the setting and early strength development of concrete"; the Canadian Standards Association (1973) describes the

chloride-type accelerator as "an admixture which accelerates the initial set of early strength development of concrete." According to the British Standards Institution (1974), an accelerator "increases the initial rate of reaction between cement and water and accelerates the setting and early strength development of concrete". The RILEM (Réunion Internationale des Laboratoires d'Essais et de Recherches sur les Matériaux et les Constructions) Committee recognizes set accelerators as having very powerful set-accelerating action but causing lower final strengths.

An accelerator, as the term suggests, increases the rate of development of certain characteristic properties of cement and concrete. It does not necessarily mean that it affects every one of them in this way simultaneously. In the chemical sense, acceleration may mean an over-all increase in the rate of reaction; in the physical sense, an increase in the rate of setting or volume change, and in the mechanical sense, an increase in the rate of development of strength. These changes may not occur at the same rate over the whole period of hydration. The same admixture may have different effects or even opposite effects depending on time, conditions of the experiment, and amount and composition of the materials.

It is generally assumed that the acceleration of cement hydration will result in a corresponding gain in strength. The heat developed during hydration gives a fair indication of the degree of hydration; the heat of hydration produced by adding different amounts of calcium chloride to cement is compared with compressive strength in Table 2. At about the same degree of hydration, the strength developed differs from one sample to another, depending on the amount of calcium chloride added. In terms of hydration, the maximum acceleration effect is achieved with 3½% CaCl₂, but with this amount lowest strength result.

Calcium chloride is generally termed as an accelerator for cement, but in the early literature it was considered as a retarder of setting of cement (Forsen 1938). (It is a retarder for high alumina cement, calcium alumino-fluorite cement, and slag cements.) Although the addition of calcium chloride accelerates setting and hardening of cement, it does not necessarily follow that when added to individual components of cement, it acts as an accelerator. For example, calcium chloride retards the hydration of the tricalcium aluminate phase, while acting as an accelerator for the hydration of the silicate phase. Triethanolamine, also known as an accelerator, may accelerate the hydration of the tricalcium aluminate-gypsum hydration while retarding the hydration of the silicate phase (Ramachandran 1974b).

TABLE 2. Heat of hydration versus compressive strength in cement pastes containing calcium chloride

Heat of reaction (cal/g)	Compressive strength (psi)			
	0% CaCl ₂	1% CaCl ₂	2% CaCl ₂	3½% CaCl ₂
10	2900	3050	3400	—
15	4800	4500	5300	2650
20	6700	6000	6900	4600

NOTES: 1 cal/g = 4,1868 J/g, 1 psi = 6,894 757 kPa.

The degree of acceleration, whether it is assessed through changes in chemical, physical, or mechanical characteristics, depends on the time interval considered for calculation. For example, in the very early periods of hydration of the silicate phase, the maximum acceleration (in terms of strength) occurs at an addition of 2% CaCl₂. However, at 30 days the paste with 5% CaCl₂ appears to have received the greatest acceleration (Table 3 (from Traetteberg and Ramachandran 1974)).

The extent to which calcium chloride changes the hydration rate of cement or cement compounds depends on the method of determination. Hydration of tricalcium silicate yields calcium silicate hydrate and lime (calcium hydroxide). If the rate of hydration is determined in terms of the silicate phase consumed, generally the degree of hydration is higher with greater percentages of added calcium chloride. If the rate of reaction is determined in terms of the lime formed, however, the accelerating effect changes with time of hydration. For example, in the hydration of tricalcium silicate the accelerating effect with different amounts of chloride at 6 h decreases in the order of 4% CaCl₂ chloride > 1% CaCl₂ > 0% CaCl₂. At longer times, the relative effects are 1% CaCl₂ > 0% CaCl₂ > 4% CaCl₂ (Ramachandran 1971a).

These implications of accelerating effect are also relevant to other changes that occur during hydration of cement, i.e. surface area, density, interconversion reactions, volume change, flexural strength, modulus of elasticity, porosity, and creep.

The Antifreezing Action

As the freezing point of a solution is less than that of a pure solvent, the addition of calcium chloride to water should result in the depression of the freezing point of water. Consequently, in text books and many other publications, the impression is given that a calcium chloride admixture acts as an antifreeze. By the addition of 0.25, 0.5, 1.0, 2.0, 3.0, 5.0, and 7.0% anhydrous calcium chloride, the freezing point of water is lowered by 0.1, 0.2, 0.4, 0.9, 1.4, 2.3, and 3.4°C, respectively (Thomas 1929). For example, if 2% calcium chloride (dihydrate) is added to cement

TABLE 3. Microhardness (kg/mm²) of tricalcium silicate paste with calcium chloride prepared at a water-solid ratio of 0.3 (Traetteberg and Ramachandran 1974)

Hydration time (days)	Microhardness (kg/mm ²)		
	Tricalcium silicate + 0% CaCl ₂	Tricalcium silicate + 2% CaCl ₂	Tricalcium silicate + 5% CaCl ₂
1	5.3	13.5	10
2	7.4	22.5	15.8
3	8.7	27.7	23.0
7	11.9	29.8	29.0
15	17.2	31.7	36.0
30	20.9	34.6	50.5

at a water-cement ratio of 0.5, the concentration of solution would be 4%. This amount would lower the freezing point by approximately 1.4°C. This shows that at normal dosages the depression of the freezing point is negligible and hence calcium chloride does not act as an antifreeze. The real effect of calcium chloride is its ability to increase the rate of reaction in the cement-water system.

Normal dosages of calcium chloride, as used in North America and most other countries, should not be considered as an antifreeze; larger additions, however, depress the freezing point of water considerably. Results have been published in the Russian literature on the use of larger amounts of calcium chloride in concrete. At larger additions, calcium chloride may indeed act as an antifreeze and hence very little cold weather protection would be needed (Table 4 (from Orchard 1973)). This does not mean an endorsement of this practice because many properties of concrete may be affected.

The Dosage

In spite of the widespread use of calcium chloride for several decades, statements in the literature about its dosage in concrete are often ambiguous or erroneous. It is possible that the use of incorrect amounts of calcium chloride may have been one of the contributing factors to many failures of concrete. It is very

TABLE 4. Recommended amounts of calcium chloride + sodium chloride required for curing concrete at different temperatures (Orchard 1973)

Calcium chloride CaCl ₂ (%)	Sodium chloride NaCl (%)	Temperature (°C)
18	5	-22.8
14	6	-20.0
8	7	-15.0
3	7	-10.0

important to know the actual dosage of chloride added to concrete because larger-than-specified amounts cause corrosion of the reinforcement. When aggregates of marine origin are used, it is essential that the total chloride present is exactly known.

A dosage expressed in terms of a certain percentage of calcium chloride would be ambiguous because it might refer to the pure anhydrous calcium chloride or to the hydrate. By purification and desiccation, a number of solid hydrates can be prepared (Table 5).

The commonly imposed limit of 2 or 1.5% calcium chloride cannot be understood unless the type of salt to be used is specified. Two per cent of the flake form, which is a hydrate containing two molecules of water, is equivalent to only 1.5% of anhydrous calcium chloride. If 2% of the anhydrous salt is tolerated then 2.65% of the dihydrate may be used.

Calcium chloride is available as pellets or other granules, flakes, or in a solution form. According to the standards, the regular flake form should contain a minimum of 77% calcium chloride (anhydrous) and the pellet or other granular forms, a minimum of 94% calcium chloride. In these two types the percentage of calcium chloride may vary depending on the purity. The use of specific language would ensure the use of the right amount. It is suggested that in the literature either the phrase "per cent calcium chloride dihydrate" or "per cent anhydrous calcium chloride" by weight of Portland cement be used, to avoid confusion.

Calcium Chloride and Corrosion

One of the most important factors to be considered in the use of calcium chloride in reinforced concrete is its possible contribution to the corrosion of steel. Not only has there been a controversy as to the advisability of using calcium chloride but also considerable confusion as to the details of the processes occurring in concrete containing calcium chloride.

In a normal reinforced concrete, cement paste provides an alkaline environment that protects embedded steel against corrosion. In concrete containing calcium chloride, however, the protective film that is normally formed cannot be maintained with the same efficiency and the potential for cor-

TABLE 5. Percentage of calcium chloride in different hydrates

Salt	Formula	Calcium chloride (%)
Calcium chloride hexahydrate	CaCl ₂ ·6H ₂ O	50.7
Calcium chloride tetrahydrate	CaCl ₂ ·4H ₂ O	60.6
Calcium chloride dihydrate	CaCl ₂ ·2H ₂ O	75.5
Calcium chloride monohydrate	CaCl ₂ ·H ₂ O	86.0
Calcium chloride (anhydrous)	CaCl ₂	100.0

rosion is increased. Even when the protective film is not perfect the reinforcing steel does not corrode to a significant extent unless oxygen has access to the steel. Of course, moisture is an important medium through which chloride, oxygen, and carbon dioxide are transported to the reinforcement. Two opposing effects are involved when steel comes into contact with a solution of calcium chloride: an increase in the corrosion rate due to enhanced conductivity of the electrolyte and a decrease in the corrosion rate by the reduced solubility of oxygen. Hence the observation that the rate of corrosion decreases at higher concentrations of chloride (Pollitt 1923). This does not mean that high concentrations should be used in concrete. At high concentrations of chlorides concrete may be very poor in strength and not pass the specification limits.

In concrete made with calcium chloride, contrary to the belief of some users, not all the chloride originally added causes corrosion. Only the soluble chloride is capable of influencing corrosion. Calcium chloride is highly soluble in water. A part of the added chloride reacts with calcium aluminate and ferrite phases to form insoluble chloride-containing compounds. Contrary to general opinion, some of it also reacts with the silica-bearing phases, forming insoluble complexes. In general, the amount of bound or immobilized chloride increases as the aluminate phase in cement is increased. Even with small additions of chloride, there is a possibility of some chloride remaining in a soluble form. Table 6 (from Wolhutter and Morris 1973) illustrates the difference in the immobilized chloride for two types of mortars containing different initial amounts of chloride.

It has also been observed that sulphate-resisting Portland cement with 1% calculated $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ leaves about four times as much chloride in solution as does the ordinary Portland cement with 9% $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ (Woods 1968). This explains why ordinary Portland cement gives better protection against corrosion than does sulphate-resisting cement (Steinour 1964).

The quantity of chloride associated with the incidence or extent of corrosion in reinforcing steel has not been established. It is difficult to establish a corrosion threshold but a figure of 0.20% Cl^- on the basis of cement has been suggested (Clear 1974). This figure is based on the assumption that approximately 75% of the total chloride extracted by wet chemical analysis exists as a free chloride. For calculation, the chloride existing in the aggregates should also be taken into account. A chloride content in excess of the threshold amount does not mean that corrosion starts automatically. It also depends on the availability of moisture and oxygen.

TABLE 6. Immobilized calcium chloride in mortars (Wolhutter and Morris 1973)

CaCl ₂ added (% by weight)	Immobilized CaCl ₂ (% basis of cement)	
	Portland cement	Portland cement and blast furnace slag
1	0.8	0.7
2	1.1	1.6
4	2.0	3.0
7	3.6	4.8
10	4.9	6.1

Corrosion in prestressed concrete is a much more serious problem than in normally reinforced concrete because of the role played by the stressed steel in the stability of the system. It has been established that steam cured prestressed concrete containing small amounts of CaCl_2 would eventually exhibit corrosion. The prohibition of chloride in prestressed concrete by some standards is practically impossible to achieve because even the mixing water, cement, admixture, and aggregate contain minute quantities of Cl^- ions. Specifications should state either that no admixture in which chloride is added or serves as an active ingredient should be used or they should impose limits of chloride concentrations.

Several methods have been suggested to protect reinforcement from corrosion. These include cathodic protection, neutralization of chlorides, water- and salt-proof membranes, polymer impregnation, and coatings. The Building Research Establishment in the U.K. is exploring the possibility of using corrosion-resistant but more expensive steels for reinforcement. The performance of more expensive austenitic stainless alloys exposed in the laboratory or at industrial and marine exposure sites to high levels of Cl^- concentrations has been excellent compared to conventional high yield steels. Precautions should be taken if austenitic steel is used in combination with normal mild steel reinforcement. If close contact occurs over a significant area, corrosion of mild steel is increased.

Possible States of Calcium Chloride

The mechanism by which calcium chloride accelerates the hardening of cement has not been established. This may be attributed to the complex chemical nature of cement and its hydration products. It appears, therefore, that it would be more beneficial to study first the effect of this admixture on the individual compounds and then extend this knowledge to binary and ternary mixtures and ultimately to cement itself. An apparently simple system to investigate would be tricalcium silicate – water – calcium

chloride. Despite much work, the exact mechanism by which the acceleration takes place even in this system is still obscure. Most of the several theories proposed imply that calcium chloride acts catalytically. In this theory there is a tacit assumption that calcium chloride remains in a free state. Recent work has cast doubts on this (Ramachandran 1971b).

One of the important questions that must be answered is: In what state does calcium chloride exist in the hydrating tricalcium silicate paste? If calcium chloride does not take part in any chemical reaction, it should exist in a free state throughout the course of the reaction. It is generally assumed that since calcium chloride is highly soluble in water, leaching the paste with water would bring into solution all calcium chloride existing in a free state. Recent studies (Ramachandran 1971b) have shown that this is not a valid assumption. Calcium chloride is soluble in alcohol. Alcohol-leached solutions are found to contain a much smaller amount of calcium chloride than that contained in the water leachate. This difference is caused by the water, which brings into solution some complexes of chloride that are not soluble in alcohol.

Several methods, such as thermal analysis, chemical analysis and X-ray diffraction, have been used to estimate and study the possible states in which calcium chloride may exist in the system tricalcium silicate - calcium chloride - water (Ramachandran 1971b). The chloride may be in a free state, as a complex on the surface of the silicate during the dormant period; as a chemisorbed layer on the hydrate surface, in the interlayer spaces, and in the lattice of the hydrate. Figure 3 gives an estimate of the states of chloride in the silicate hydrated for different periods. The results show that the amount of free chloride drops to about 12% within 4 h, becoming almost nil in about 7 days. At 4 h, the amount of chloride existing in the chemisorbed and (or) interlayer positions rises sharply and reaches about 75%. Very strongly held chloride that cannot be leached even with water occurs to an extent of about 20% of the initially added chloride. Since this is not easily soluble in water, it would not be available for corrosion processes. The literature does not take into account this possibility when evaluating the corrosion of reinforcing steel in the presence of calcium chloride in concrete. Many other effects, such as acceleration of hydration, increase in surface area, morphological changes, and inhibition of formation of afwillite (a crystalline form of calcium silicate hydrate), in the presence of calcium chloride may be related to the formation of various chloride complexes in this system.

Addition of calcium chloride to cement or calcium silicates influences various physical, chemical, and

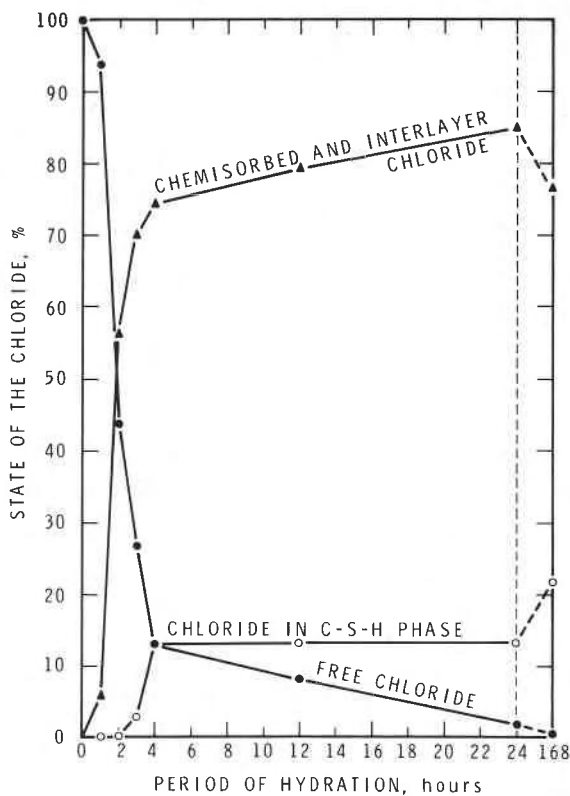


FIG. 3. Possible states of chloride in tricalcium silicate hydrated to different periods (Ramachandran 1971b).

mechanical properties. Many theories have been proposed to explain these effects. Some of these theories attempt to explain one phenomenon and others attempt to deal with several. It is reasonable to conclude that no one mechanism can explain all the effects of calcium chloride, such as changes in kinetics of hydration, mechanical strengths, surface area, morphology, chemical composition, porosity, and density. Possibly a combination of mechanisms may be operating, depending on the materials, experimental conditions, and period of hydration. Future work should be directed to the investigation of this possibility.

The Intrinsic Changes

The use of calcium chloride in concrete technology is based on its ability to increase the rate of setting and strength development in concrete. These time-dependent properties have been studied extensively and in almost all publications major efforts have been directed to a comparison of the relative properties of concrete with or without calcium chloride after a particular curing time. These are very useful but from a basic and characterization point of view the comparisons should be based on some intrinsic property of the system. They could be based on equal

degrees of reaction (hydration) or equal porosity. A comparison of strengths at equal porosity values has revealed many new facts in cementitious systems (Beaudoin and Ramachandran 1975). For example, among the systems magnesium oxychloride, Portland cement, gypsum, and magnesium hydroxide, it appears that magnesium hydroxide forms the strongest body at a porosity of about 30%.

The question as to whether the changes in properties of concrete in the presence of calcium chloride are just due to the degree of hydration or to the change in the intrinsic structure of the cement paste has yet to be answered. Very little work has been done on this aspect. In the early stages of reaction in cement pastes, the paste with 2% CaCl_2 shows a higher strength than the sample without calcium chloride, although both are hydrated to the same extent. This difference narrows at higher degrees of hydration. At equal degrees of hydration, the sample with 3½% CaCl_2 shows the least strength (Table 2).

The surface area of tricalcium silicate phase containing calcium chloride is much higher than that without calcium chloride. In a tricalcium silicate paste hydrated to 65% (hydrated for 28 days without calcium chloride and 12 h with 2% CaCl_2) the chloride-treated paste shows lower water surface area ($261 \text{ m}^2/\text{g}$) than the reference paste without chloride ($324 \text{ m}^2/\text{g}$); at a hydration degree of 86%, the surface area of the former remains the same ($270 \text{ m}^2/\text{g}$) (Skalny *et al.* 1971).

A concrete containing calcium chloride shows a higher shrinkage than plain concrete, especially at early periods of hydration. The larger shrinkage at earlier periods can be attributed mainly to a larger degree of hydration. The differences in shrinkage may not be the same if the results are compared at the same degree of hydration. In the hydrated alite (tricalcium silicate phase containing MgO and Al_2O_3), at equal degrees of hydration (up to 60%), alite containing 1% CaCl_2 shows a larger shrinkage (25–40% more) than that containing no chloride (Berger *et al.* 1976). With increasing hydration, the shrinkage of alite + 1% CaCl_2 paste decreases steadily, whereas that of alite + 0% CaCl_2 increases.

The porosity and pore-size distribution also may show differences. At equal degrees of hydration, alite + 0% CaCl_2 shows a greater volume of pores with a diameter $>0.0065 \mu\text{m}$ than the sample with 1% CaCl_2 (Berger *et al.* 1976).

These examples show that at equal degrees of hydration, pastes containing calcium chloride exhibit different properties from those containing no chloride. The full significance of these observations has yet to be established.

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