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Review Research

A REVIEW STUDY OF THE USE OF CALCIUM CHLORIDE IN CONCRETE

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Abstract: For several decades, calcium chloride has been widely used as a cheap and effective accelerator. Calcium chloride is remarkably decreasing the initial and final setting times of concrete. It is mainly used at low-temperature concreting because it allows for earlier finishing and reduces the effects of water freezing inside fresh concrete. The use of calcium chloride in reinforced concrete has been decreased after identifying its effect on reinforcement corrosion. However, calcium chloride is still widely used in ordinary concrete and some reinforced concrete in specific proportions. This paper reviews the most important mechanical and chemical effects of calcium chloride on concrete mixtures, its effects on reinforcement corrosion, the conditions of its use, and its mechanism of action. This review study highlights the need for a detailed study to verify calcium chloride's exact role in reinforcement corrosion and the maximum permissible limits for its use in reinforced concrete. In addition, there is a need to study the compatibility of calcium chloride with other concrete admixtures.

Keywords: *Calcium chloride; accelerators; concrete admixtures; early strength*

1. Introduction

The setting of concrete slows down when the ambient temperature is below 21°C. The significance of the effects increases when it approaches freezing temperature. The low temperature also delays the process of cement hydration and therefore takes a long time to harden. Calcium chloride is used in cold weather concreting to overcome this problem or when high early strength of concrete is required (i.e. emergency concrete works) [1-3]. Therefore, the main cause why concrete contractors use accelerators is to control the concrete's initial and final setting times [4]. Ordinary concrete accelerators make up about 4 percent of all admixtures sold in Europe according to the European Federation of Concrete Admixture Associations. Calcium chloride is the oldest admixture used for ordinary Portland concrete; its use dates back to 1886 [1]. It is a by-product of the manufacturing process of sodium carbonate. Therefore, it is a widely available and cheap material. Calcium chloride is classified as a type C admixture according to ASTM C 494-10.

2. Effects of Calcium Chloride on Physical and Mechanical Properties of Concrete

2.1. Setting Time

Calcium chloride is remarkably decreasing concrete's initial and final setting times [5-7]. It is mainly used at low-temperature concreting because it allows for earlier finishing and reduces the effects of water freezing inside fresh concrete. Therefore, it is not recommended in hot weather concreting because it accelerates the setting of the concrete, making transporting,

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pouring, and finishing concrete extremely difficult [8-9].

The Canadian standards (CSA A266.2-1978) and American standards (ASTM C494 – 05) involve that calcium chloride should reduce the initial setting time by not less than 60 minutes and not more than 180 minutes (CSA) or 210 minutes (ASTM) in comparison to the control mix.

There is no significant reaction between calcium chloride and cement paste in the period from 2 to 6 hours [10-12] after mixing, although a quick setting can happen in this period.

2.2. Water/Cement Ratio

Calcium chloride does not play a role in reducing the water requirements to yield a particular slump, and therefore, no increase in compressive strength is expected at 28 days of age. There are some claims of calcium chloride producers that it increases the workability of concrete, but there is no scientific evidence to support this claim. However, it may reduce the bleeding of concrete due to its early setting and hardening [11].

2.3. Compressive Strength

When calcium chloride is used as an accelerator admixture in the concrete, it increases the rate of hardening of the concrete [13,14]. ASTM C-494 requires a minimum increase of 125% over the control sample at age of 3 days. At 6 or 12 months of age, the requirements are only 90% of the control sample. The increase in strength as a result of adding calcium chloride in the first 72 hours ranges from 30 to 100% [1]. The addition of amounts of CaCl2 higher than acceptable standards reduces the strength [2]. It should be noted that accelerators are in low demand nowadays, particularly in the precast concrete industry, where there are other means to achieve high early strength, such as using very low water/cement ratios by the use of superplasticizers [15]. However, accelerators continue to be in demand when placing concrete at low temperatures.

Bruce Roy et al. [16] studied the effect of using calcium chloride in the production of concrete blocks. Different amounts of calcium chloride were used in the study with a maximum inclusion rate of 4% of cement weight. It was concluded that the compressive strength increased with the inclusion of calcium chloride in the mix at all ages and even at 28 days of age, whereas the water absorption of the blocks increased with the inclusion of calcium chloride in the mix.

Benjamin et al. [17] performed laboratory, and field tests using calcium chloride in soil-cement mixtures. The effects of calcium chloride dosage, temperature and time on the unconfined compressive strength of soil cement were studied. It was concluded that calcium chloride increases the unconfined compressive strength of soil-cement at curing temperatures in the range (of 2°C and 21°C). The strength decreased dramatically in temperatures exceeding 50°C.

2.4. Flexural Strength

The addition of CaCl2 increases flexural strength to a lesser degree compared to the induced increase in compressive strength [18-20]. The ASTM C-494 specification includes at least a 10% increase in flexural strength should be obtained at the age of 3 days compared to the control sample. At later ages, the flexural strength may be less than the strength of the control sample.

2.5. Entrained Air

Adding $CaCl_2$ to fresh concrete does not cause air entrainment [21,22]. But, when it is used with an air-entraining admixture, it increases the air content with a lesser amount of air-entraining admixture [23].

2.6. Freezing and Thawing

Adding calcium chloride to concrete increases concrete's resistance to early frost attack damage by reducing the free water content of the mixture and causing the concrete to harden quickly. However, at later ages (see Fig. 1), the concrete containing calcium chloride is less resistant to freezing and thawing [24-26].

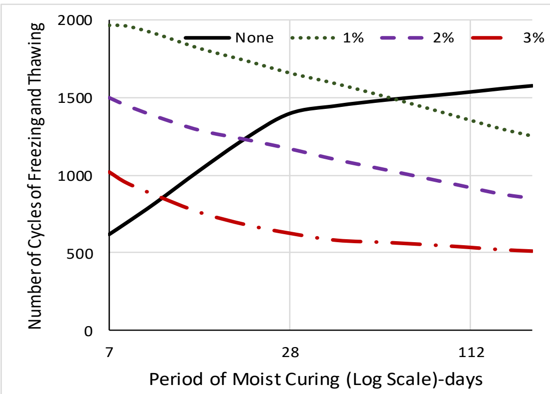

Figure 1. Freezing and thawing resistance of concrete cured at 4 °C for different calcium chloride contents [27]

When calcium chloride is used in ordinary dosages recommended for concrete, it will not lower the freezing temperature and therefore cannot be considered an antifreeze material [26,28-30].

2.7. Resistance to Erosion and Abrasion

Calcium chloride has been found to increase concrete's resistance to erosion and abrasion, and this increase continues for all ages [27].

2.8. Drying Shrinkage

Calcium chloride increases the drying shrinkage by 10 to 15% or more [27, 31]; its extent is affected by the percentage of calcium chloride, the cement type, and the curing period. There are also some indications that the creep of concrete may also increase with the addition of calcium chloride. Because calcium chloride increases drying shrinkage, its use in patching materials should be avoided as deboning between the patching material and substrate will most likely happen. Therefore, the PCI design handbook for precast and prestressed concrete does not recommend its use in patching repair materials [32].

2.7. Efflorescence

White deposits are formed on the surface of the hardened concrete in some cases as a result of the use of calcium chloride in concrete [33]. However, under normal exposure conditions, calcium chloride attracts water and often does not cause efflorescence as is the case with other salts. These white deposits are insoluble in water and can be removed with dilute hydrochloric acid.

3. Effects of Calcium Chloride on Chemical Concrete Properties

3.1. Resistance to Sulfate Attack

Calcium chloride affects concrete when exposed to sulfate solutions. Sulfate reacts with aluminum and calcium ions in cement paste producing calcium sulfate and calcium sulfate hydrate, causing trouble in the concrete. The presence of calcium chloride in concrete reduces its resistance to sulfate attack [21, 22].

3.2. Heat of Hydration

The generation of heat of hydration is faster when calcium chloride is present in the mix, mainly in the initial 10 to 12 hours [5,34]. Although calcium chloride does not increase the total amount of heat generated by the hydration process, it significantly affects the hydration process by causing heat to develop faster and in about half the normal time [9]. For example, the heat of hydration is about 30% greater than the reference concrete during the first twenty-four hours. This contributes to increasing the value of calcium chloride in cold concrete works, as early heat release helps in reducing the effects of freezing, earlier finishing, and removal of forms. Fig. 2 shows the effect of calcium chloride and calcium formate in the evolution rate of the heat of ordinary Portland cement with a water/cement ratio of 0.5 and at 20°C.

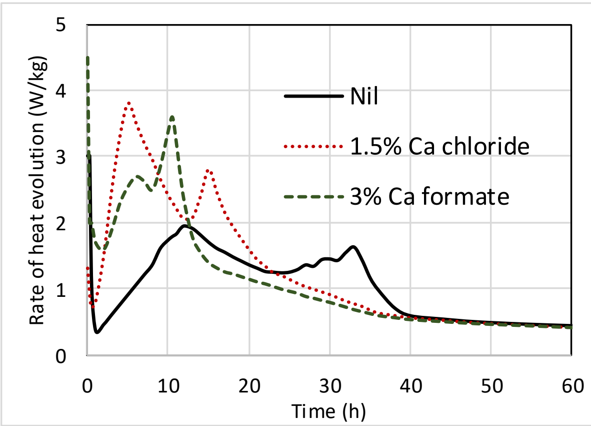

Figure 2. The heat evolution rate of OPC with Calcium chloride and Calcium formate [23].

3.3. Alkali-Aggregate Reaction

When using highly alkaline cement with a specific type of aggregate, swelling of the aggregate causes concrete deterioration. The use of calcium chloride exacerbates the reaction between the cement and aggregates. If the use of calcium chloride is necessary, expansion can be reduced by using low-alkali cement, pozzolanic materials, or chemically stable aggregates [21, 35].

3.4. Resistance to Corrosion of Reinforcement

The chloride ions present in $CaCl_2$ in concrete stimulate the corrosion of metals and steel reinforcement [36-40]. It is prohibited to use calcium chloride in prestressed concrete because of the high corrosion rate due to the large wire surface area and the stress differences are larger. Calcium chloride is not recommended for steam-cured concrete. ACI 318 code [41] does not allow prestressed concrete or aluminum embedment--containing concrete to use calcium chloride or other chloride-containing admixtures. Therefore, calcium chloride cannot be used in post-tensioned concrete containing aluminum conduits.

The ACI 318-19 code comprises conditions of the allowable ratios of chlorides in concrete. Therefore, Chapter 4 of the ACI 318-19 code can be used to determine the possibility of adding calcium chloride and the amount that can be added. However, it is difficult to determine the extent of calcium chloride admixture that can be added while adhering to the maximum soluble chloride ions because concrete components contain different amounts of chlorides depending on the suppliers [42-44]. As a rule, in class C0 exposure according to the ACI 318-19 exposure categories (Table 19.3.1.1), calcium chloride can be added by about 2% of the cement weight. In class C1 exposure the ratio is about 0.5%. For a concrete subject to the class C2 exposure category, it is rarely possible to add any calcium chloride to concrete. These rules should however be confirmed by the concrete supplier.

The ACI Code does not allow calcium chloride to be used in concrete exposed to soil or groundwater containing sulfate in an amount classified as exposure category S2 or S3. Because the chloride content limits in concrete are intended to prevent corrosion of the reinforcement, these limits do not apply to slabs-on-grade that do not contain a reinforcement. Also, these limits are used for uncoated rebar. The chlorine content can be determined according to ASTM C 1218.

Obinna and Nemkumar [45] studied whether the previously observed positive effects of calcium chloride mixed with acrylic polymer on the durability of concrete could include protection of steel reinforcement from corrosion and resistance to acid attack. In this study, the effect of adding 0.5-1.5% of calcium chloride polymer mixture by weight of cement on the corrosion of steel reinforcement was evaluated by accelerated corrosion test. The results of the research indicated that Calcium chloride-blended acrylic polymer is not suitable for use as a chemical admixture in cement composites reinforced with steel bars as it expedites rebar corrosion. But, it can be used as a chemical admixture in non-reinforced uses such as mass concrete dams, rigid pavements, walkways, and industrial floors that are subjected to harmful chemical effects.

In a discussion presented in [46] by Berntsson and Chandra, it is mentioned that very rare conditions of reinforcement corrosion can be directly attributed to the use of calcium chloride in concrete, and the calcium chloride dosage was 3 to 4% by weight of cement in these cases. According to Butler, the calcium chlorides of low levels can hardly be responsible for major reinforced concrete distress. Some other researchers have concluded that $CaCl_2$ does not significantly corrode rebar if the concrete is well-designed and well-compacted and if the reinforcement concrete cover is suitable [14].

Pruckner and Gjørv [36] studied the influence of using different types of chlorine compounds on the corrosion of steel reinforcement. Mortars with ordinary Portland cement were prepared to which different ratios of calcium chloride and sodium chloride were added. Corrosion is tested mainly by electrical resistance and acid capacity measurements.

It was concluded that when calcium chloride was used in fresh mortar, the pH level decreases, the acidic capacity of calcium hydroxide decreased, and the acidic capacity of CSH increased. All of these factors aggravate the corrosion of rebar.

Since free chloride stimulates the corrosion of reinforcement, Ramachandran et al. [47] studied the immobilization of chloride by different types of cement. It was concluded that cement with high C3A had lower free chlorides than ordinary Portland cement.

Janutka et al. [48] conducted research on the corrosion resistance of steel fibers and reinforcing bars in cement mortars containing $CaCl_2$ admixture in proportions from 2 to 10 percent by weight of cement. The corrosion rate was examined by the electrochemical potential method. Scanning electron microscopy was used to examine the steel surfaces and the mortar structure. The electrochemical potential measurements indicated corrosion of the reinforcing bars by adding 2 percent $CaCl_2$ in ordinary reinforced mortars, while the use of steel fibers did not indicate any harmful corrosion of the bars until the $CaCl_2$ content reached 6 percent. Therefore, a conclusion was made that the addition of $CaCl_2$ admixture to concrete may be less harmful to reinforcing bars in steel fiber reinforced concrete than in ordinary reinforced concrete.

The presence of fibers in concrete can prevent the occurrence of cracking and lead to a decrease in crack width [49]. And due to the relationship between crack width and concrete permeability, FRC is more resistant to water penetration and steel corrosion than conventional concrete under cracked conditions [50,51]. Naidu and Joseph [52] in a review study of the corrosion behavior of fiber-reinforced concrete, concluded that the fibers bind the chlorides and prevent their transfer through the concrete, and the fibers delay the appearance of corrosion in reinforced concrete members provided that the applied load does not exceed a certain limit.

3.5. Compatibility with Other Admixtures

There are many claims by calcium chloride producers that it is compatible with other concrete admixtures. However, there appears to be no scientific research to support these claims.

4. Methods of Adding $CaCl_2$ to the Concrete Mix

Calcium chloride is obtainable in the form of pellets, flakes, granules, or in solution form. The ordinary flakey form contains at least 77% calcium chloride, while pellets and granulated forms contain at least 94% calcium chloride. Since all of the calcium chloride forms are soluble in water, a solution form is usually recommended for its use [7].

Attention should be paid that the calcium chloride solution not coming into direct contact with cement, as this leads to a rapid set of cement [53]. Therefore, it is recommended to dilute it with water and mix it with rubble. Attention should be paid that the solution does not come into direct contact with the cement, as this leads to a rapid set of cement. Therefore, diluting it with water before mixing with the other constituents is good practice.

Calcium chloride is easily soluble in cold water with constant stirring. The correct way to dissolve calcium chloride is to add calcium chloride to water, not add water to calcium chloride [7]. Hot or warm water should never be used to dissolve calcium chloride. The solution should be allowed to cool before use.

The process of adding calcium chloride should be to the aggregate in the mixer as part of the mixing water during mixing. The mixing water should be reduced by an amount equal to the volume of the added calcium chloride solution.

5. Acceleration Mechanism of $CaCl_2$

Regarding the acceleration mechanism using calcium chloride, Rosenberg [10] indicated that acceleration is primarily a catalytic factor and that the C3S component is most affected. The chemical reaction between C3A and CaCl2 forms 3CaO. Al2O3. CaCl2 xH2O has little influence on the early hydration of cement. C3A first reacts with gypsum preferentially, and after the completion of this reaction, calcium chloride begins to act significantly [54,55]. There is evidence that a chloride compound may be present in the hydrated C3S compound. However, CaCl2 appears to act primarily as a catalyst for C3S and C4AF hydration [43, 56-58]. In high w/c ratios, the chloride ions react to form hydrochloraluminate, and stabilize the ettringite composition [21].

During the hydration process, the presence of $CaCl_2$ causes the formation of small fibrous crystals indicating a rapid crystallization, which may be due to the high ionic character of the water phase in the presence of $CaCl_2$ [59].

Hydration of the compound C3A - $CaCl_2$ - $CaSO_4.2H_2O$ indicates that $CaCl_2$ mainly catalyzes the reaction between C3A and $CaSO_4.2H_2O$.

The sulfates react first, then the reaction of C3A and chloride begins after the consumption of gypsum. $CaCl_2$ is thought to stabilize ettringite formation. After the stabilization of ettringite, hydrates with a hexagonal structure, (i.e. $C3A.Ca(OH)_2.12H_2O$, $C3A.CaCl_2.10H_2O$ and $C3A.CaSO_4.20H_2O$) produce solid solutions.

Mathilde et al. [58] used X-ray Micro-Tomography analyses with 0.325 µm pixel size to study the early hydration process of slag-based blended cement with and without calcium chloride. It was concluded that calcium chloride accelerates the dissolution of OPC and increased hydrates precipitation between the first 6 and 11 hours of hydration. The effect was stronger in the period between 24 - 31 hours of hydration. The dissolution/precipitation reaction in the absence of calcium chloride was slower and was not visible until 24 hours after the hydration.

6. Conclusions

This review study highlights the main effects of calcium chloride on concrete. Calcium chloride is used to reduce the initial and final setting times of concrete in addition to being a hardening accelerator. Calcium chloride affects other properties of concrete such as drying shrinkage, air entrainment, freezing and thawing, resistance to erosion and abrasion, and other mechanical and chemical properties. This review presents the effects of calcium chloride on the fresh and hardened properties of concrete. To date, no accelerator competes with calcium chloride in terms of cost and effectiveness. However, due to its role in reinforcement corrosion, some countries have restricted its use in reinforced concrete, and others have prohibited its use. Its use in plain concrete is still very popular. The production of an efficient, inexpensive, and chloride-free accelerator remains a challenging problem. Therefore, it was concluded that it is necessary to study the reconsideration of the use of calcium chloride in reinforced concrete and determine the proportions of its use with the addition of corrosion inhibitors to concrete. It was also concluded that there is a need to study the compatibility of calcium chloride with other concrete admixtures.

Conflict of Interest

The author declares that there are no conflicts of interest regarding the publication of this manuscript.

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