

Technical Note on the Properties, Use, and Analysis of Calcium Chloride as a Swimming Pool Plaster Admixture

by onBalance
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What is Calcium Chloride?

Calcium chloride (CaCl_2) is an additive (or “admixture”) which is added to the basic components of swimming pool plaster (cement, sand aggregate, and water) in order to speed up the initial time required to set cement. This allows pools to be plastered even in cooler weather, when set times may otherwise be extended too long. It also allows for a single crew to plaster more pools per day. Calcium chloride may be added in flake, prill, or liquid suspensions.

Unfortunately, using calcium chloride has effects other than just the speeding up process:

- Although calcium chloride speeds initial set times, it retards or inhibits later set processes
- It introduces additional porosity to the bulk cement paste, and increases permeability
- It promotes discoloration

Extensive research in the cement industry has shown that calcium chloride is a primary causative factor in the discoloration and shrinkage of concrete (for example, see Greening and Landgren 1966). Calcium chloride has also been implicated in the spot etching, discoloration, crazing, and shrinkage of swimming pool plaster, as shown in the case histories released to date by onBalance. Although discoloration and shrinkage begin when any amount of calcium chloride is added, the consensus has been that, absent other compounding factors, the degree of discoloration and shrinkage is acceptable when the amount of calcium chloride added does not exceed 2% by weight to the cement.

Factors which compound the detrimental effects of calcium chloride in swimming pool plaster have been shown to include overfinishing the surface (excessive hard trowelling) and the practice of adding water to the surface during finishing operations. These factors have been shown to cause the same compounding effects in other concrete flatwork (again, for example, see Greening and Landgren 1966).

Because of the potential problems that calcium chloride may cause, extensive experimentation has been performed in the cement industry to study its effects. As a result, the consensus of the studies has been that calcium chloride should not be used unless necessary, and if used, the dosage should never exceed 2% calcium chloride to the cement by weight (and only if compatible with all other admixtures).

When things go wrong

If insufficient calcium chloride is added to a batch, the only real downside is that it will take longer to finish troweling the plaster surface. However, if too much calcium chloride is added, it can cause the following problems:

- Rapid setting, requiring special care in the placement and finishing operations
- Excessive porosity in the bulk cement paste

- Excessive cracking in the paste and on the surface
- Nodule growth on the cracking
- Excessive discoloration, especially light and dark discoloration patterns
- Coping practices by the finishers, such as hard troweling and retempering, which introduce additional problems such as trowel burn and spot etching

How much calcium chloride was added?

Once a pool is plastered, there are times when failure analysis is required. Regarding calcium chloride, there are a number of ASTM-approved methods for determining the chloride content of hardened cementitious products, including:

- SEM analysis of the microstructure, specifically including the presence of secondary reaction materials associated with excess calcium chloride
- Spectrophotometric analysis, also looking for those byproducts as well as for the actual chloride content
- Titration for acid soluble chlorides

OnBalance uses a field adaptation of ASTM Method 1152/C, the Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete. The adaptation involves substituting the use of a chloride titrator – specifically, the Hach Quantab® titrators for chloride (Cl⁻), which utilize the silver nitrate/potassium chromate method described in AWWA Standard Method 4500-Cl-B (Chloride/Argentometric Method), in place of ASTM Test Method C 114, a laboratory titration. This field substitution is described in the literature (see Pullar-Strecker 1987), and has been shown to provide consistent results which closely match the results of laboratories (including RJ Lee Group and Construction Technologies Laboratories) following the full titration protocol or one of the other ASTM methods.

The cement laboratories we work with also use this method, but also employ SEM/EDS analysis.

Summary of Method

Here is a summary of the method as onBalance has performed it in its lab:

1. Acquire about 0.5 to 1 cubic inch of material to be analyzed
2. Pulverize the sample material into a fine powder, using a mortar and pestle, and place 10 grams of the powder in a beaker
3. Add 50 ml of 4:1 nitric acid to the beaker, and agitate the sample until all foaming has ceased
4. Adjust the pH of the sample to the 6-8 range using NaOH
5. Top the solution up to 100 ml with distilled water
6. Test the chloride level using a Hach/ETS Quantab titrator
7. Record the results as “ppm Cl⁻ in a 10g/100ml solution”

There are several other ways of ascertaining the endpoint in this test – including a buret titration method (where the technician looks for a color change as the endpoint) and a titration using a chloride ion selective probe to ascertain the endpoint.

Reporting Test Results

Calcium chloride content may be expressed in a number of ways. Primarily, these include giving the percentage of chloride ion in the bulk solid, or giving the chloride content in parts per million (ppm) of a solution containing dissolved material. ASTM C 1152, for example,

involves dissolving 10 grams of the cementitious solid in 100 ml of an acid solution, and analyzing the chloride in solution in terms of ppm. Both forms of result, %Cl⁻ in bulk and ppm Cl⁻ in solution, have been shown by exhaustive ASTM standards to be accurate. Calculations must then be applied to either of these results to equate them to the customary percent calcium chloride dihydrate by weight to cement.

When converting analysis results on swimming pool plaster to percent calcium chloride dihydrate by weight to cement, care must be taken to use correct information and/or assumptions about both the standard and the bulk plaster.

First, it is understood that many forms of calcium chloride are used in the pool industry, including 77% dihydrate flake, 94% anhydrous prill, and 29% liquid suspensions of calcium chloride. Raw test results reflect the chloride ion (Cl⁻) content of the plaster, but the standard (not to exceed 2% by weight to cement) is expressed in terms of dihydrate (see ACI 212.3R-99 Chemical Admixtures for Concrete, section 3.8). Conversion of the test results must, then, equate to the dihydrate (CaCl₂•2H₂O) standard.

To put this in perspective, in a batch of pool plaster containing four 94 pound bags of cement (a total of 376 pounds of cement), regardless of the amount of sand and water added, the maximum amount of calcium chloride dihydrate that may be added is 7.52 pounds, which equates to:

- 5.8 pounds of 100% pure calcium chloride
- 6.2 pounds of 94% prill or powder calcium chloride
- 7.5 quarts of 29% liquid calcium chloride

Second, since the standard compares the chloride content only to the cement portion of the solid, the aggregate and water percentages of the hardened product must either be known, determined by analysis, or assumed. When giving chloride results, onBalance assumes a 1:1.5 cement:aggregate ratio and a 1:0.3 cement:water ratio, unless specific information is available to show or suggest that these ratios vary in the given sample.

The 1:1.5 cement:aggregate ratio is fairly standard in the industry, and leaner mixes (i.e., up to 1:1.75) do not alter results to a substantial degree.

The 1:0.3 cement:water ratio is consistent with known cement science relative to the amount of water required to hydrate cement. Although additional water is used to constitute the plaster, often up to 0.5 and 0.6, excess water does not remain as part of the resultant solid mass.

To convert “% chloride ion (Cl⁻) in bulk solid” to “% calcium chloride dihydrate (CaCl₂•2H₂O) by weight to cement” multiply the first figure by 5.7:

Assumptions:

Bulk plaster is 1:1.5 cement:aggregate
Bulk plaster is 1:0.3 cement:water

1 unit cement
1.5 units aggregate
0.3 units water
2.8 units total bulk plaster weight

$$\begin{aligned} \text{CaCl}_2 \text{ is } 63.89\% \text{ Cl}^-, \text{ or chloride: } & 40.08 \text{ Ca}^{2+} + 35.453 \text{ Cl}^- + 35.453 \text{ Cl}^- = 110.986 \text{ CaCl}_2 \\ & 35.453 \text{ Cl}^- + 35.453 \text{ Cl}^- = 70.906 \text{ Cl}_2 \\ & 70.906 \div 110.986 = 63.887\% \end{aligned}$$

Calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) has a listed strength of 77%

When the %Cl⁻ as weight percent of a sample is determined, convert that amount to percent calcium chloride dihydrate, or %CaCl₂•2H₂O (the product the universal "2% maximum calcium chloride by weight to the cement" is derived from) by applying the following formula:

$$\begin{aligned} & \text{_____ (weight \% Cl}^- \text{ in bulk plaster)} \\ \times & 2.8 \quad \text{(volume of total plaster per single volume of cement)} \\ \div & 0.639 \quad \text{(percent of calcium chloride that is actually chloride)} \\ \div & 0.77 \quad \text{(strength of product)} \\ = & \text{_____ percent calcium chloride to weight of cement} \end{aligned}$$

Since $2.8 \div 0.639 \div 0.77 = 5.69$, a simplified and rounded shortcut is to multiply the "weight % Cl⁻ in bulk plaster" by 5.7 to get the percent calcium chloride to weight of cement.

When analyzing "Core Sample #2" (from oB-00004), RJ Lee determined the sample to contain 0.45% Cl⁻.

$$\begin{aligned} & 0.45 \quad \text{(weight \% Cl in bulk plaster)} \\ \times & 2.8 \quad \text{(volume of total plaster per single volume of cement)} \\ \div & 0.639 \quad \text{(percent of calcium chloride that is actually chloride)} \\ \div & \underline{0.77} \quad \text{(strength of product)} \\ = & 2.56 \quad \text{percent calcium chloride dihydrate to weight of cement} \end{aligned}$$

$$\text{or, } 0.45 \times 5.7 = 2.56$$

That means that the plasterer added just over 2½% calcium chloride dihydrate by weight of cement to the plaster.

To convert "ppm chloride ion (Cl⁻) in a 10g/100ml solution" to "% chloride ion (Cl⁻) in bulk solid" divide the first figure by 1000:

When analyzing the above-mentioned sample from oB-00004, onBalance determined the sample to contain 439 ppm Cl⁻ when 10 grams of plaster were dissolved into 100 ml of acid solution.

$$\begin{aligned}
 & 439 \quad (\text{ppm Cl}^- \text{ in a 10g/100ml solution}) \\
 \div & \quad \underline{1000} \\
 = & \quad 0.439 \quad (\text{weight \% Cl}^- \text{ in bulk plaster})
 \end{aligned}$$

To convert “ppm chloride ion (Cl⁻) in a 10g/100ml solution” to “% calcium chloride dihydrate (CaCl₂•2H₂O) by weight to cement” divide the first figure by 1000 and then multiply by 5.7:

$$\begin{aligned}
 & 439 \quad (\text{ppm Cl}^- \text{ in a 10g/100ml solution}) \\
 \div & \quad 1000 \\
 \times & \quad \underline{5.7} \\
 = & \quad 2.50 \quad (\text{percent calcium chloride dihydrate to weight of cement})
 \end{aligned}$$

Many researchers have lamented the lack of standardization in the past relative to the expression of chloride content in relation to the 2% limit (see, for example, Ramachandran 1976). OnBalance echoes that lament, and notes that even their own data has been rendered in different forms in published work. To avoid confusion, in all future publications, onBalance will follow the ACI 212 protocol of providing either “ppm chloride ion in a 10g/100ml solution” or “% chloride ion in bulk solid” results as ascertained by analysis, and rendering them in terms of % calcium chloride dihydrate. For clarification, the accompanying Table lists onBalance project numbers, along with the % calcium chloride dihydrate (CaCl₂•2H₂O) content of the analyses.

Please note that although each lab was testing plaster from the same pool, they were not necessarily testing plaster from the same batch of plaster, since samples from various parts of the pool may have originated from different batches. However, all samples were taken from spot etched areas of those pools.

References

- American Concrete Institute. *Manual of Concrete*. “ACI 212.3R – Chemical Admixtures for Concrete.”
- American Society for Testing and Materials. *Annual Book of ASTM Standards*. “ASTM Method 1152 C – Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete.”
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- American Water Works Association. *Standard Methods for the Examination of Water and Wastewater*. AWWA Standard Method 4500–Cl⁻ B (Chloride/Argentometric Method)
- Greening, N. R. and R. Landgren. *Surface Discoloration of Concrete Flatwork*. Published as Portland Cement Association Research Bulletin RX-203
- Pullar-Strecker, Peter. *Corrosion Damaged Concrete – assessment and repair*. Construction Industry Research and Information Association, Essex, England, 1987
- Ramachandran, V. S. (Vangipuram Seshachar) “Concrete Admixtures Handbook”

oB-00003 (Acton CA)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.47		2.7
onBalance		439	2.5

oB-00004 (Phoenix AZ)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.45		2.6
onBalance		439	2.5

oB-00005 (ES)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.38		2.2
onBalance		460	2.6
Micro-Chem (top)	0.336		1.9
Micro-Chem (bottom)	0.361		2

oB-00005 (M)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.32		1.8
onBalance		428	2.4

oB-00015 (Phoenix AZ)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	1.04		5.9
onBalance		1036	5.9
CTL	1.063		6

oB-00017 (Skinner 1)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.97		5.5

oB-00017 (Skinner 2)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.67		3.8
onBalance		581	3.3

oB-00018 (NPC #10)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	1.3		7.4
onBalance		837	4.8

oB-00019 (Prevost)			
	wt % in bulk	ppm 10g/100ml	calc % c:cc-H2O
RJ Lee Group	0.69		3.9
onBalance		746	4.2