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ADMIXTURES FOR SHOTCRETE GROUTS, FILLING VOIDS, AND NUCLEATION KINETICS OF CALCIUM CHLORIDE

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NUCLEATION KINETICS OF THE ADMIXTURE CALCIUM CHLORIDE

by

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Abstract

Of the several missions assigned to TRB committee (A2E05) "Chemical Additions and Admixtures for Concrete", the most interesting one perhaps is "the elucidation of admixture reaction kinetics."

What follows is such elucidation. It pertains to the admixture calcium chloride, and is excerpted from a paper which was formally presented at 65th Annual Meeting of the TRB, titled "Use of Calcium Chloride Accelerated High Early Strength Concrete for Slab Repair and Replacement," by John W. Bugler of the New York State Department of Transportation (Region 10-Hauppauge, NY 11788).

The Accelerating Admixture - Calcium Chloride

The Chemistry - Background. The major reaction products of hydration of alite [substituted tricalcium silicate (C_3S)] are calcium silicate hydrate, ($3CaO\ 2SiO_2\ 3H_2O$) or abbreviation C-S-H and calcium hydroxide, $Ca(OH)_2$ or abbreviation CH. The C-S-H is largely a microcrystalline amorphous gel of enormous surface area (500 m^2/g) and occupies about 70% (volume) of the hydrated material. The calcium hydroxide is crystalline and occupies about 20% (volume) of the hydrated material. They are formed as follows:

$C_3S + H \rightarrow$ C-S-H + CH

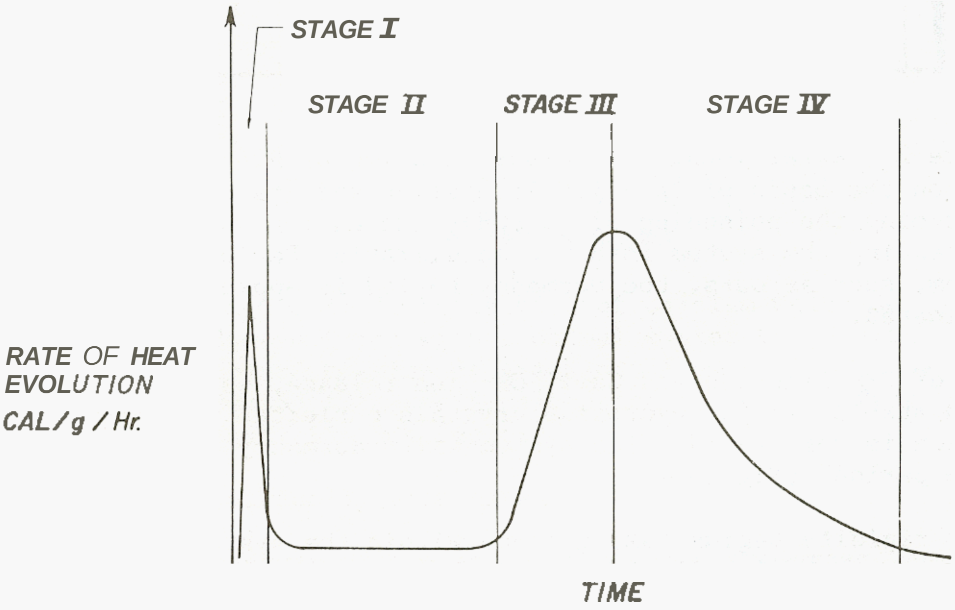
Tricalcium Silicate + water → Calcium Silicate Hydrate + Calcium Hydroxide

$$2(3CaO\ SiO_2) + 6H_2O \rightarrow 3CaO\cdot 2SiO_2\cdot 3H_2O + 3Ca(OH)_2$$

The calcium silicate hydrate provides the cohesive matrix responsible for strength development, and as such is the reaction product most responsible for the engineering properties of portland cement.

The Chemistry - Kinetics. The first step in the hydrolysis of C_3S appears to be one mole of H_2O for one mole of CaO, a very rapid reaction. Hydrolysis proceeds by an attack of water on the surface of the cement grains, causing the reactive components to pass into the ionic state. Cat+ and OH- ions rapidly approach levels of high concentration. A solution close to saturation with respect to calcium hydroxide is quickly formed. Cat+ and OH- ions are now leached from C3S into a solution of increasing chemical potential. This makes their continued release more difficult. As a result, the reaction rate slows down and the system enters the "dormancy period" (Figure 1 and 2).

While in the dormancy period the ion concentration slowly approaches and passes into supersaturation. In approximately 2-1/2 hours, a level of supersaturation 1.5 to 2.0 times the saturation level is achieved, enabling stable calcium hydroxide crystals to nucleate, take form, and commence to precipate out of solution at a very rapid rate (Figure 2).



STAGE I	A brief initial period of reactivity, 5 minutes, then a tapering off of 5 minutes, then entry into the Dormancy Period.
STAGE II	The Dormancy Period. Two hours in length for our system without $CaCl_2$ and heated wafer. For a properly designed accelerated system such as the one under discussion. the Dormancy Period is virtually eliminated (reduced usually to thirty minutes).
STAGE III	The Acceleration Period, where there is renewed reaction and very rapid hydration of C_3S, formation of C-S-H gel and $Ca(OH)_2$. For the system under discussion if usually lasts 3.5 hours. Most of the C_3S is hydrated. Compressive strength is close to 3000 psi.
STAGE IV	The Deceleration Period. The reaction rate slows down and is osmosis diffusion controlled.

Figure 1 Heat liberation curve of hydrating C3S as determined by isothermal condition calorimetry. (After Kondo and Daimon [4])

The precipating $Ca(OH)_2$ crystals act as a sink for Ca++ and OH- ions in solution; and as such causes them to flow rapidly to, and become incorporated into the newly formed crystal. The solution's ionic concentration level drops. This in turn, enhances the further dissolution and reaction of C_3S.

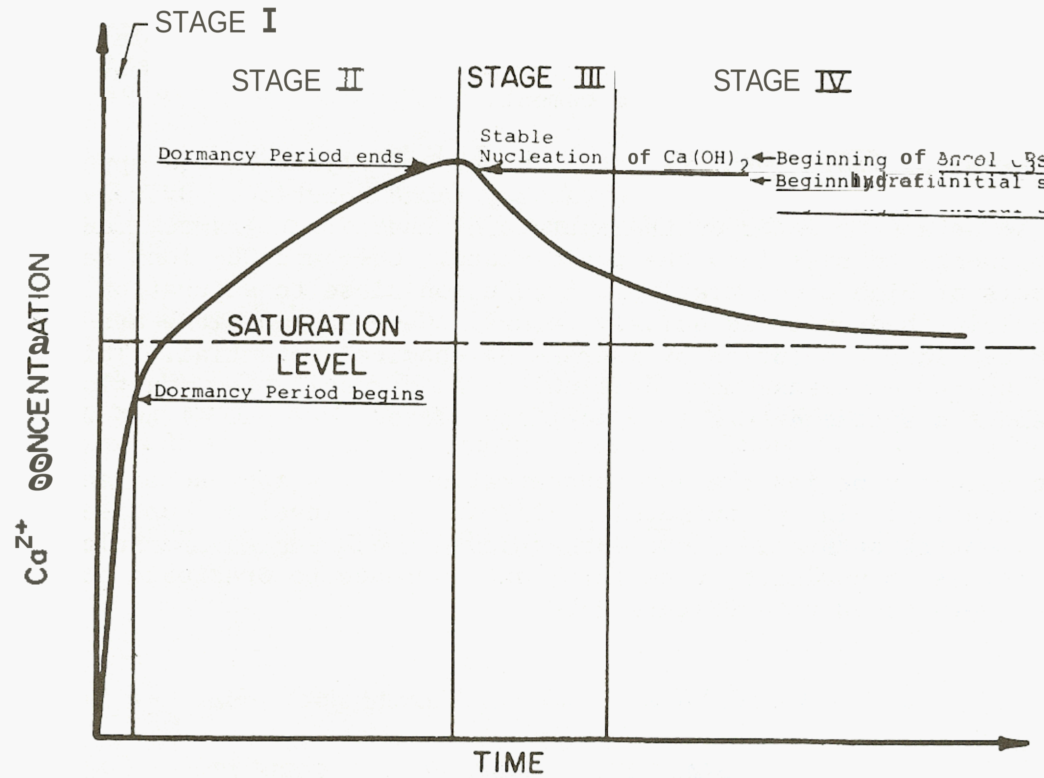


Figure 2 (After Young) [3] Classification of Hydration stages of C_3S, on the basis of Ca++ ion liberation and its effects in overcoming the poisoning of Ca $(OH)_2$ nucleation and crystal growth; and leading the system into the Acceleration Period. In a $CaCl_2$ system, such as ours, the Dormancy Period is appreciably shortened or eliminated.

The new rate of C_3S reaction and Ca++, OH- ion release, is controlled by the rate at which stable calcium hydroxide crystals nucleate, take form, precipate and grow; which is very rapid. The system exits dormancy and enters the "acceleration period" (Figure 1).

A concomitant rigidity begins taking place within the system as stable reaction products take form as calcium silicate hydrate and calcium hydroxide. This rigidity is "initial set."

Discussion One would expect that once the Ca++, OH- ionic concentration levels had surpassed saturation, that equilibrium would be re-established by crystallization. But, such is not the case for at least two hours. Why? According to Nate Greening [2] and reported by Francis Young [3], free silicate ions, present in small, but not insignificant quantity, absorb onto the nuclei of newly formed calcium hydroxide crystals, and poison their growth. Until the level of supersaturation (with regard to Ca++, OH- ion concentration) is sufficiently large enough to overwhelm and overcome that poisoning effect, the system will remain in the dormancy period and no rapid reaction rates will take place.

Calcium Chloride. "Any compound that hastens the nucleation and growth of $Ca(OH)_2$ will act as an accelerator. Calcium chloride is the most effective accelerator, because it supplies more calcium ion per unit weight. At equal molarities, different calcium salts have similar accelerating powers [3]. The time required for a normal system to achieve an ion concentration level of sufficient magnitude to overwhelm and overcome the poisoning effects described is approximately 2-1/2 hours.

However, through the addition of calcium chloride, the system is literally swamped with calcium ions. This almost immediately brings about the equivalent supersaturation level necessary to overwhelm and overcome the poisoning effects described thereby enabling the system to exit dormancy and enter the acceleration period in approximately thirty minutes (Figure 3).

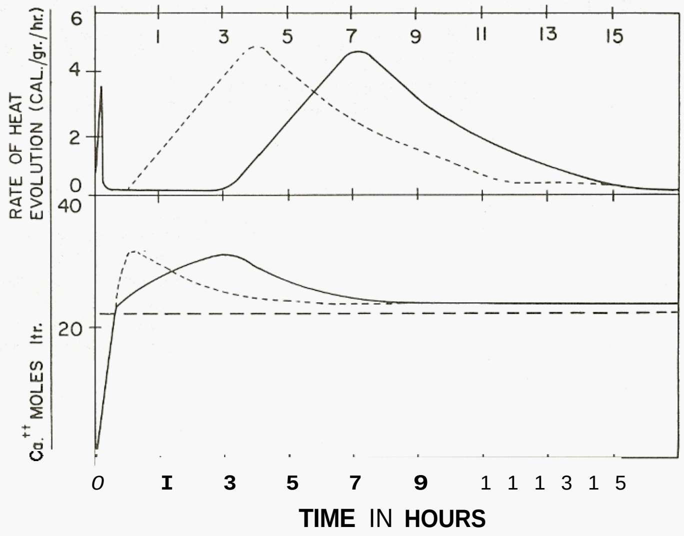


Figure 3 Juxtaposition of Calcium Chloride System (---) with a normal system (—) with regard to time of break out from the Dormancy Period into the Acceleration Period. (After Young [3] and Bugler)

The dormancy period is virtually eliminated.

It is the continuing endeavor of committee (A2E05) to encourage research into reaction kinetics of admixtures, and in *so* doing, we welcome continued outside discussion, input and support.

References

1. J. Skalny, J. F. Young. Mechanisms of Portland Cement Hydration. 7th International Congress on Cement Chemistry. Paris 1980.

2. Former Director of Research. Cement Division. Ideal Basic Industries. Fort Collins, Colorado

3. J. F. Young. Reaction Mechanisms of Organic Admixtures With Hydrating Cement Compounds. Transportation Research Record 564. TRB, 1976.

4. R. L. Kondo and M. Daimon. Early Hydration of Tricalcium Silicate. A Solid Reaction With Induction and Acceleration Periods. Journal Of The American Ceramic Society, Volume 52, 1969.