# Chemical Admixtures for Concrete

ACCELERATORS

Özge Andiç Çakır, PhD

# Accelerators: Definition

- An accelerating admixture is a material that is added to concrete for reducing the time of setting and accelerating early strength development.

# Accelerators: Classification

- Accelerating admixtures,
- Water-reducing and accelerating admixtures

# Usage

- Accelerating admixtures are used in cold water concreting operations and also are components of antifreezing admixtures and shotcreting mixes.
- In cold weather concreting, there are other alternatives;

- use of rapid-hardening cement,
- use of higher than normal amount of ordinary portland cement,
- warming of the concrete ingredients.

# Advantages of Using Accelerators

- efficient start and finishing operations,
- reducing the period of curing and protection,
- earlier removal of forms so that the construction is ready for early service,
- plugging of leaks,
- quick setting when used in shotcreting operations.

# Types and Chemistry

1. Water-soluble inorganic salts that include chlorides, bromides, fluorides, carbonates, thiocyanates, nitrites, nitrates, thiosulfates, silicates, aluminates and alkali hydroxides that accelerate the setting of portland cement;
2. Water-soluble organic compounds such as triethanolamine (TEA), calcium formate, calcium acetate, calcium propionate and calcium butyrate.
3. Quick setting admixtures used in shotcrete applications and which promote setting in a few minutes and may contain sodium silicate, sodium aluminate, aluminum chloride, sodium fluoride, strong alkalis and calcium chloride;
4. Miscellaneous solid admixtures such as calcium aluminate, seeds of finely divided portland cement, silicate minerals, finely divided magnesium carbonate and calcium carbonate

# Calcium Chloride, Disadvantages

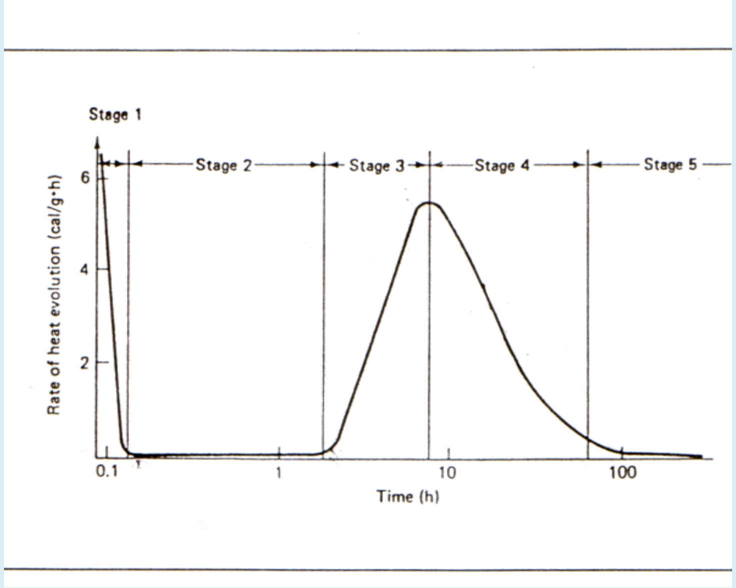
- Promote corrosion of metals in contact with concrete due to the presence of chloride ions,
- Increased creep and drying shrinkage of concrete,
- Reduction of the resistance of concrete to sulfate attack.

# Calcium Chloride Debate

- There is considerable disagreement and even misunderstanding on the effect of calcium chloride on many properties of concrete.
- For example, whereas in some countries, including Europe the use of calcium chloride is prohibited, in some others, such as Canada and the USA, the use of calcium chloride is permitted provided certain precautions are taken.
- However, calcium chloride is economical and also the most efficient of all accelerators.
- Attempts have continued to find an effective alternative to calcium chloride because of some of the problems associated with its use.

# Mechanism of Action

# Calorimetric Curve of $C_3S$ Hydration




- Stage 1: A period of rapid evolution of heat, which stops within about 15 minutes.
- Stage 2: A period of relative inactivity, the dormant period, which is the reason why portland cement concrete remains in the plastic state for several hours. Initial set occurs in 2 to 4 hours, about the time $C_3S$ has begun to react again.
- Stage 3: The silicate continues to hydrate rapidly, reaching a maximum rate at the end of the acceleration period. By this time final set has been passed and early hardening has begun.
- Stage 4: The rate of reaction again slows down,
- Stage 5: It reaches a steady state within 12 to 24 hours.

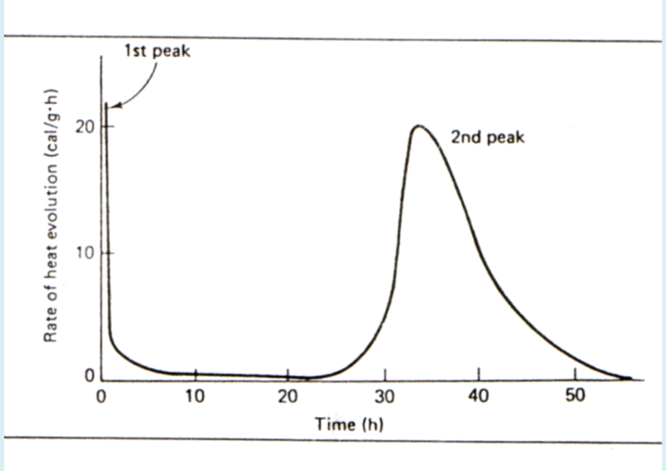
# Mechanism of Action: Water-soluble Inorganic Salts

When calcium salts are used:

- They increase the rate of hydration of $C_3S$ compound in cement.
- Generally, the dormand period is shortened, but the rate of hydration during the following stages may be increased.

# Calorimetric Curve of $C_3A$ Hydration

- Both steps in hydration of $C_3A$ are exothermic. The formation of ettringite slows down the hydration of $C_3A$ by creating a diffusion barrier around $C_3A$ analogous to the behavior of C-S-H during the hydration of calcium silicates. This barrier breaks down during the conversion to monosulfoaluminate and allows $C_3A$ to react rapidly again. The calorimeter curve for $C_3A$ hydration which is given Figure looks like that of $C_3S$ although the reactions are much different and the amount of heat evolved is much greater.
- The first heat peak in Figure is completed in 10 to 15 minutes but the time necessary for the second peak to occur depends on the amount of sulfate available in the system. The more gypsum there is in the system, the longer the ettringite will remain stable.
- In most cements, the conversion of ettringite to monosulfoaluminate takes 12 to 36 hours, after all the gypsum has been used to form ettringite.



# Mechanism of Action: Water soluble organic salts

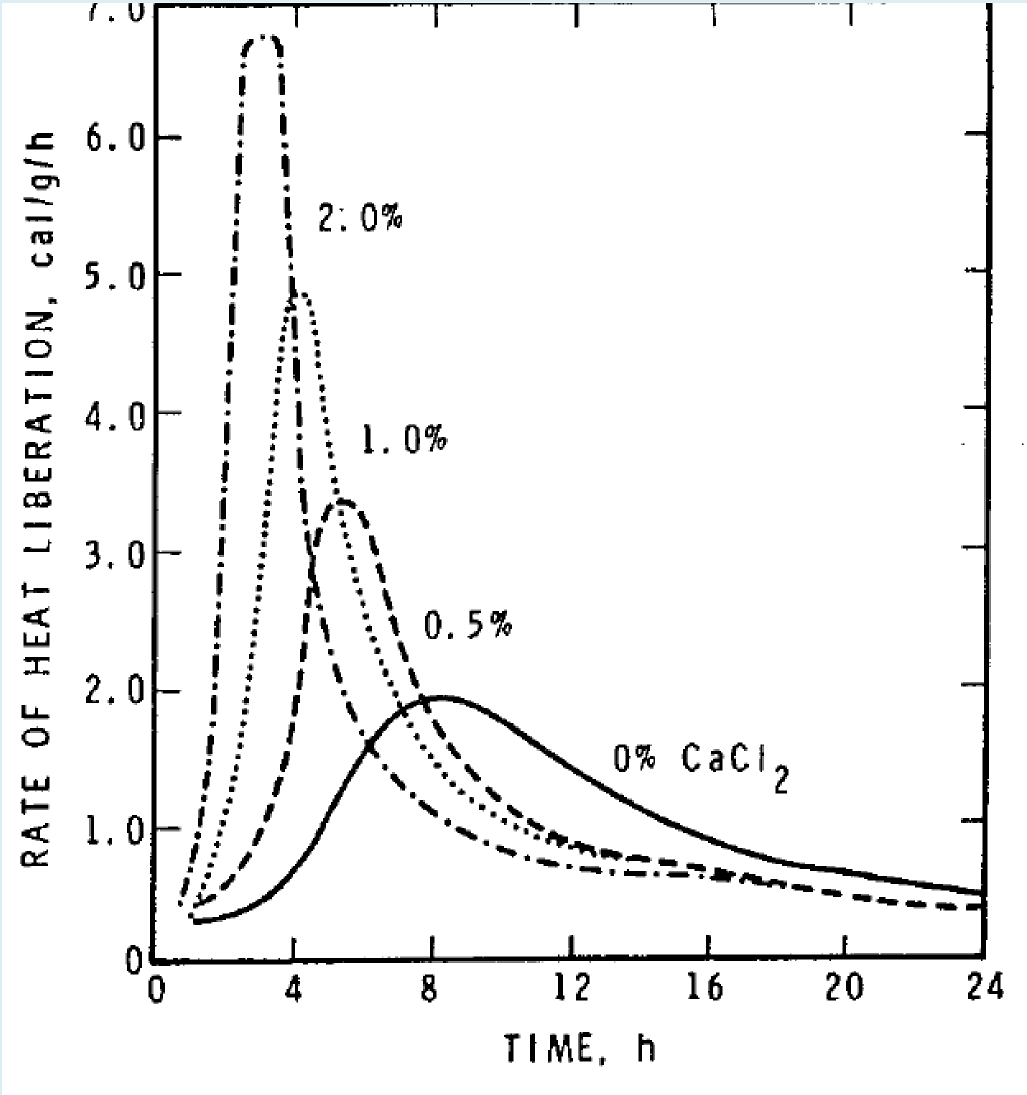
- Most of the organic accelerators are believed to act by increasing the rate of hydration of the $C_3A$ compound of cement.
- Quick setting organic admixtures can cause flash setting of $C_3A$ by promoting very rapid hydration in contact with water.

# Mechanism of Action: Miscallenous Solid Admixtures

- Various silicate minerals have been found to act as accelerators.
- Finely divided silica gels accelerate the strength development by accelerating the C3S compound of cement.
- Very finely divided magnesium carbonate and calcium carbonate are also found to be beneficial in decreasing the setting time of concretes.

# Effects on Cement Hydration

- The hydration of cement, being an exothermic reaction, produces heat if the hydration is accelerated, heat is produced at a faster rate.
- This is particularly significant in the first 10-12 hours and is of considerable importance in cold weather concreting.



# Effects on Cement Hydration

- The amount of heat generated depends on the temperature of curing.
- The lower the temperature of hydration, the lower is the amount of heat developed.
- However, if the sample contains $CaCl_2$ there is an acceleration of hydration and more heat is developed at a particular temperature.
- The heat developed due to $CaCl_2$, is especially significant at lower temperatures of curing.

# EFFECTS ON PROPERTIES OF FRESH CONCRETE

# Fresh Concrete Properties- Effect of Accelerators

- Accelerating admixtures based on calcium chloride, formate, nitrate, and thiocyanate have no significant effect on the workability, air content, mix stability, or water–cement ratio of concretes into which they are incorporated.
- The only properties of plastic concrete which are affected are the heat evolution and setting time.

# Workability

- It is generally observed that addition of $CaCl_2$, increases slightly the workability and reduces the water required to produce a given slump of concrete.
- In combination with an air-entraining agent, $CaCl_2$, may sometimes improve further the workability. A small increase in air content and average size of air voids may also result.

# Setting Characteristics

- Calcium chloride reduces significantly both the initial and final setting times of concrete. This is useful for concreting operations at low or moderate temperatures. It permits quicker finishing and earlier use of slabs.
- The setting times are decreased as the amount of $CaCl_2$, is increased. Excessive amounts e.g., 4-5% may cause rapid set and hence should be avoided.
- Even using the same type of cement but obtained from different sources shows differences in setting characteristics.
- There is no direct correlation between the acceleration of setting and subsequent strength development in the hardened state.
- Most of the other accelerators behave in a similar way to calcium chloride. The early heat evolution increases with the use of calcium chloride and other accelerators. However, the total heat liberated at 28 days and beyond is not changed appreciably.

# Air Entrainment

- Accelerators do not have adverse effects on air entrainment although trial batches should be used to check this.
- Some accelerators may require additional water if early stiffening occurs. However, they can be formulated with a water-reducing admixture.

# Bleeding

- Bleeding is usually reduced when setting time is decreased.
- Segregation is not affected by accelerators.

# EFFECTS ON PROPERTIES OF HARDENED CONCRETE

# Strength

- Conventional accelerators are expected to substantially increase the compressive strengths at early ages (1 and 3 days).
- The actual values depend:

- on the amount of accelerator added,
- the mixing sequence,
- temperature,
- curing conditions,
- W/C ratios,
- the type of cement.

- The long term effect of accelerators on the strength development in concrete is not clearly established, some reporting higher strength while others reporting lower strength.

# The increase in compressive strength of concrete containing calcium chloride is greater at lower temperatures

| *Curing temperature (°C)* | *Increase in compressive strength at 28 days over plain concrete (%)* |
|---|---|
| –10 | 90 |
| 0 | 25 |
| 10 | 16 |
| 20 | 12 |
| 40 | 7 |

# The effect of calcium nitrite on strength development

| Admixture (%) | Compressive strength (N mm²) | | |
|---|---|---|---|
| | 1 day | 7 days | 28 days |
| 0 | 9.0 | 23.5 | 34.7 |
| 2 | 11.1 | 31.3 | 39.5 |
| 3 | 13.5 | 34.2 | 40.7 |
| 4 | 15.8 | 36.8 | 44.0 |
| 5 | 16.3 | 36.7 | 44.8 |

# Influence of calcium formate on the compressive strength of concrete

| | Compressive strength (% of reference) | | | |
|---|---|---|---|---|
| *Calcium formate* | *1 day* | *7 days* | *28 days* | *1 year* |
| 1.0 | 136 | 123 | 115 | 110 |
| 2.0 | 152 | 131 | 107 | 103 |

# Frost Resistance

Accelerators usually help to produce smaller air bubble sizes and smaller spacing factors in air-entrained concrete which lead to a desireable air-void system for frost resistance of concrete.

# Sulfate Resistance

- Calcium chloride reduces the sulfate resistance of concrete made with non-sulfate resistance portland cement.
- However, when sulfate resistant portland cement is used, the addition of calcium chloride does not adversely affect sulfate resistance.
- The effects of non-cloride accelerators should be investigated with respect to their effect on durability.

# Corrosion of Reinforcement

- Calcium chloride has been widely investigated for their effect to promote high early strength and also its effect on corrosion of reinforcing steel.
- There is no universal agreement about the levels of calcium chloride that should be tolerated.
- There is a general agreement that no calcium chloride should be added to the mixture in prestressed concrete or conventionally reinforced concrete which will be exposed to moisture and chlorides in service.

# Corrosion of Reinforcement

- ACI Committee has determinbed that the maximum acid-soluble chloride ion content, expressed as a percent by weight of cement should not exceed 0.08% for prestressed concrete and 0.20% for all reinforced concrete.
- When it is preferred to avoid chlorides, alternative admixtures are usually used.

# Volume Stability

Materials that accelerate calcium silicate hydration generally increase shrinkage at early ages. The long term shrinkage may/may not be affected significantly.

| Samples | 7 | 14 | 28 | 84 | 168 |
|---|---|---|---|---|---|
| | Days | | | | |
| | % Shrinkage | | | | |
| Reference | 0.013 | 0.021 | 0.030 | 0.049 | 0.056 |
| $CaCl_2$, 2% | 0.023 | 0.033 | 0.045 | 0.056 | 0.068 |
| TEA, 0.033% | 0.016 | 0.029 | 0.040 | 0.056 | 0.064 |
| Ca Formate, 3% | 0.015 | 0.025 | 0.036 | 0.054 | 0.056 |

# CONCLUSION: BENEFICIAL AND DETRIMENTAL EFFECTS

# Beneficial Effects

- Reduce the time of setting. Thus, provide:
  - Early finishing of surfaces,
  - Reduction of pressure on forms
- Increase initial rate of strength development. Thus provide:
  - Earlier removal of forms,
  - Reduction of the required period of curing and protection,
  - Partial or complete compensation for the effects of low temperatures in strength development,
  - Earlier completion of a structure or repair.

# Detrimental Effects

- Since the time of handling, placing and finishing of the concrete is cut down, there may be serious problems if reliable scheduling of construction operations is not done,
- Excessive dosage rates may excessively reduce the setting time or produce flash set,
- May increase drying shrinkage at early ages,
- May slightly reduce strength in the long term,
- May aggrevate corrosion of reinforcement.

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http://www.basf-yks.com.tr/TR/urunler/KatkiSistemleri/betonkatkilari/Pozzutec1/Documents/pozzutec_1.pdf

# SET RETARDERS

# Definition

- A “retarder” or “retarding admixture” is an admixture that lengthens setting time and workability time of fresh concrete.

# Utilization

- The delay in setting time of concrete may be a vital necessity in many structures such as in hot weather concreting or when extended time for concrete placement, vibration and finishing is required.

# Chemistry

Retarding admixtures are based on:

- The organic compounds include unrefined Na, Ca, or $NH_4$ salts of lignosulfonic acids, hydroxycarboxylic acids (Na, Ca or triethanolamine salts of some acids), and carbohydrates.
- Inorganic compounds such as oxides of Pb and Zn, phosphates, Mg salts, fluorates and borates also act as retarders.

# The Mechanism of Retardation

- The mechanism of retardation is again based on adsorbtion of retarding admixture on the surface of the cement particles.
- The large admixture anions and molecules that are adsorbed on the particles hinder further reaction between cement and water, that is, they retard setting.
- They slow down the rate of early hydration of $C_3S$.
- Later, as a result of the reaction between the admixture salts and $C_3A$ from the cement, the salts are removed from the liquid phase system, thus eliminating further retardation.
- Subsequent hydration may be more rapid so that strength development need not be much slower than in unreacted paste if retardation is not excessive.

# Mechanism of Retardation

The effect of lignosulfonate on cement depends not only on the amounts of $C_3A$ and $C_3S$ but also on the alkalis, the $SO_3$ content, the particle size of cement, etc.

Depending on these factors, early set may be retarded or accelerated but the final set is generally retarded.

The early acceleration of set is promoted in cements with higher aluminate/$SO_3$ ratios.

At early times, due to the adsorption of lignosulfonate on $C_3S$, $Ca(OH)_2$ is not released and the rate of formation of ettringite is increased.

This implies that the $C_3A$+gypsum reaction to form ettringite is faster than that containing $Ca(OH)_2$.

Table 2. Setting Characteristics of Mortars Containing Lignosulfonates

| Admixture Type | Amount (%) | Initial Setting Time (Hrs) | Final Setting Time (Hrs) |
|---|---|---|---|
| Nil | —— | 5 | 9 |
| Commercial | 0.1 | 7 | 12 |
| Sugar-Free (Na) | 0.1 | 7 | 12 |
| Sugar-Free (Ca) | 0.1 | 7 | 12 |
| Commercial | 0.3 | Quick Set | 13.5 |
| Sugar-Free (Na) | 0.3 | 12 | 15 |
| Sugar-Free (Ca) | 0.3 | 14 | 16.5 |
| Commercial | 0.5 | Quick Set | 22 |
| Sugar-Free (Na) | 0.5 | 23 | 28 |
| Sugar-Free (Ca) | 0.5 | 22 | 27.5 |

# Retardation- Effect of Temperature

- The retardation in initial and final setting times, caused by a given amount of admixture, may be different at different temperatures if the retarding effect is expressed in hours.
- However, if the number of hours of the initial and final set of the admixture-treated concrete is expressed as a percentage of the number of hours required for the reference mix to reach the same degree of setting, the retardation caused by the admixture is not significantly different at different temperatures

**Table 2.** Typical Characteristics of Concrete without and with a Commercial Retarder. (Cement content = 300 kg/m$^3$; retarder dosage = 0.3% by weight of cement; slump = 65 ± 5 mm.)

| Mix | Control Mix | | | Mix With Retarder* | | |
|---|---|---|---|---|---|---|
| Temperature, °C (°F): | 5° (41°) | 20° (68°) | 35° (95°) | 5° (41°) | 20° (68°) | 35° (95°) |
| w/c ratio | 0.58 | 0.60 | 0.61 | 0.56 | 0.57 | 0.58 |
| Setting Time** (hr:min): | | | | | | |
| Initial | 11:05 | 5:05 | 3:30 | 13:30 (+22%) | 6:10 (+21%) | 4:30 (+24%) |
| Final | 16:55 | 7:50 | 6:20 | 19:05 (+13%) | 8:55 (+14%) | 7:15 (+15%) |
| Compressive Strength (N/mm$^2$): | | | | | | |
| at 3 days | 8.2 | 15.5 | 18.3 | 7.4 | 16.1 | 19,1 |
| at 28 days | 35.0 | 35.3 | 34.1 | 40.7 | 43.3 | 41.2 |

* Figures in brackets indicate the percentage increasein the setting time caused by the admixture in comparison with the reference mix.

** Mortar has been wet-screened from concrete mix using No. 4 sieve.

# Effects of Set Retarding Admixtures on Concrete Properties

- The setting time of concrete is much shorter under hot climate conditions (high temperature, low-relative humidity, wind) than under normal conditions.
- The shortened setting time introduces a lot of problems in placing, vibrating and the finishing of concrete.
- The use of retarding admixtures provides the possibility of prolonging the setting time of fresh concrete.
- This can avoid complications when uncontrollable delays occur between mixing and placing.

# Effects of Set Retarding Admixtures on Concrete Properties

- Prolonging the plasticity of concrete may be an advantage especially in placing mass concrete. Successive lifts of concrete can be placed and vibrated without causing the occurance of cold joints that may occur if the first layer hardens before the next is placed.
- Concrete that has set but has acquired little strength is liable to microcracking when the next pouring alters the amount of form deflection.
- Keeping the concrete plastic and prolonging the plastic period can permit the concrete to adjust itself to form deflection and to eliminate microcracking.

# Effects of Set Retarding Admixtures on Concrete Properties

- In the presence of retarders concrete may remain plastic enough to be vibrated several hours after placing, thus reducing the number of air pockets and cold joints.
- A significant improvement in the finishing characteristics of a continuously placed tunnel lining was observed, due to the retarding effect of lignosulfonate admixture.

# Effects of Set Retarding Admixtures on Concrete Properties

- The available period between casting and trowelling operations of the surface of concrete slabs becomes longer when retarders are used. This is very useful in the finishing operation of large slabs.
- This characteristic is particularly important in hot weather, where a proper amount of admixture can adequately delay setting times.
- However, in hot weather the concrete surface may *dry* out and these admixtures do not prevent the formation of a crust on the concrete surface. Under these conditions, careful and prolonged curing is required in order to obtain a uniform set in the whole concrete slab; otherwise, due to the retarding effect, the concrete below the surface crust will be rolled under the weight of the heavy mechanical trowel causing the surface crust to crack.

# Effects of Set Retarding Admixtures on Concrete Properties

- Retarders, and water-reducing and retarding admixtures can increase plastic shrinkage by retarding setting, unless concrete is protected from loss of moisture.
- Only if cracks are caused by early accelerated hydration of cement, (hence rapid heat development) retarders and water-reducing and retarding admixtures may solve the cracking problem.

# Retarders-Beneficial Effects

- Delays the setting of concrete during hot weather. Thus, offsets the effects of high temperatures which decrease the setting time.
- Extends time for concrete placement, vibration and finishing.
- Avoid complications when unavoidable delays may occur between mixing and placing the concrete.
- Prolongs the plastic period of the concrete and thus enables the concrete to resist cracking due to form deflections (settlement of the forms) as the concreting proceeds.

# Retarders-Detrimental Effects

- Excessive dosage may excessively delay hardenining of concrete,
- Increases bleeding.

Any Questions?

# FOR REFERENCE BOOKS SEE COURSE SYLLABUS