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EFFECTS OF CHEMICAL ADMIXTURES ON CONCRETE DURABILITY

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Abstract

Water reducers, and in particular superplasticizers, may be advantageously used to improve concrete durability against many chemical attacks. However, in some specific cases, particularly in cold weather, sulfate salt, CaCl_2 and NaCl can damage concrete structures very severely even if a low w/c ratio has been adopted. A combined addition of superplasticizer and fly ash or silica fume allow the production of durable concrete even in such particular cases.

Air-entraining agent are used to manufacture frost resistant concrete, provided some requirements are met. *In practice* there are difficulties to meet such requirements at the job site, so that concrete structures have been deteriorated even in the presence of air-entraining agents. Intensive research work is necessary in the future to find a definitive solution to produce frost resistant concrete structure.

Key words: Chemical admixture, Plasticizer, Superplasticizer, Air-entraining agent, Durability, Workability, Sulfate attack, Chloride attack,

1. Causes of concrete deterioration

The durability of concrete is the ability of the material to last and resist the aggressive actions of the environment. The reasons of concrete deterioration can be divided into two categories: intrinsic causes of the material - due to its quality - and external causes due to ambient conditions. The problem of constructing with durable concrete can be solved, therefore, by assessing the aggressive conditions of the environment and choosing a level of adequate durability for the concrete.

The choice of an adequate level of durability must be proportioned to the type of structure. As a matter of fact, in the same environmental aggressive conditions and with the same durability of the material, the serviceability of the structure can be more or less compromised according to the size, the thickness of cover over reinforcement and the use the structure has been designed for. For instance, the serviceability of a structure deteriorated only on its surface can be negatively affected if it is a floor slab, but the same deterioration can be negligible if it is a vertical panel of the same size. On the other hand, the removal of 20-30 mm of concrete has negligible consequences in a massive structure having a thickness of several metres, but can cause disasters in a thin structure with a 20-30 mm cover. These two causes of deterioration, due to the material or the environment, can be, in turn, divided into other causes, as schematically shown in Table 1.

Table 1. Main causes of concrete deterioration

Due to the material	Due to the environment
<p><i>Inadequate Concrete Composition</i> (water/cement ratio, aggregate/cement ratio and air void system)</p> <p><i>Inadequate Workability</i> of concrete during placing</p> <p><i>Inadequate Curing</i> of concrete after demoulding</p>	<p><i>Chemical causes:</i></p> <ul style="list-style-type: none"> - sulphate; - carbon dioxide - inorganic acids (if pH is below 5, concrete requires a protective coat); - alkali; - chloride. <p><i>Physical causes:</i></p> <ul style="list-style-type: none"> - freezing and thawing, - drying process (shrinkage), - high temperatures <p><i>Mechanical causes:</i></p> <ul style="list-style-type: none"> - abrasion, - erosion, - cavitation

2. Parameters affecting concrete durability

Concrete durability mostly depends on its permeability. If the material is watertight, aggressive agents present in water cannot penetrate into it, and therefore concrete is durable. The permeability and, consequently, the durability of concrete depend on the presence of voids in the conglomerate. When voids are connected each other - because of their large number and size - a continuous porosity is present inside the material, thus making concrete in aggressive ambient permeable and deteriorable. The problem of making a concrete impermeable, therefore durable, is to obtain a discontinuous porosity which does not allow aggressive agents to permeate the material.

Concrete basically has two types of voids which are responsible for the permeability of the material: capillary pores (with a diameter varying between 0.01 and 10 μm) in the cement paste which coats aggregates, and macrovoids, having a much greater size (0.1 to 10 mm), of fresh concrete, between cement paste and aggregates due to the faulty compaction of fresh concrete.

2.1 Influence of water/cement ratio on concrete durability

Let us assume that fresh concrete has been compacted adequately, so that the capillary

pores in the cement paste are the only voids present. The volume of these pores basically depends on the water/cement ratio (w/c) of the mix and on the cement fraction (a) that reacted with water. The lower the water/cement ratio, the lower the distance among cement grains will be and less porous will be the microstructure of the hydration products. On the other hand, the higher the degree of hydration (a), the higher the volume of the cement hydration products will be and, therefore, the lower the capillary porosity will be. The equation [1.0] shows how the volume (V_p) of capillary pores (expressed in litres per 100 kg of cement) varies as a function of the w/c ratio and of the degree of hydration (a).

$$V_p = 100 w/c - 36.15 a \quad [1.0]$$

The lower the V_p value, the higher the probability that capillary pores are segmented will be, so that the watertightness and durability of concrete are attained. As it can be deduced from the equation [1.0] a decreased capillary porosity can be obtained by lowering the w/c ratio and by increasing the degree of cement hydration (a), that is, prolonging the concrete curing time. The higher the w/c ratio, the longer the curing time must be, in order that segmentation of capillary pores and, therefore, impermeability of concrete are obtained.

2.2 Influence of workability on concrete durability.

Workability is a characteristic of fresh concrete and it indicates the ability of the mixture to be placed. The more workable the mix, the easier and quicker the placement will be. Workability can also affect significantly the properties of hardened concrete.

It has already been said that concrete qualities, and particularly durability, improve as the w/c ratio lowers. Yet, if an extremely low w/c ratio was adopted to guarantee durability, workability could be inadequate to ensure a complete compaction of fresh concrete, and therefore, all the aspects concerning capillary porosity which were considered in the previous section, would simply become theoretical exercises. In fact, taking into consideration job-site operating conditions, a hardly workable mix would produce a concrete with a large number of big cavities and the problem of capillary pores would become incomparably negligible. Designers must realize that they cannot refuse to specify workability, if they really want to guarantee the durability of concrete structures. Generally speaking, concrete workability during placing must be the higher, the more difficult is the execution of the work.

2.3 The influence of curing on concrete durability

Another important aspect to guarantee concrete durability is the curing of concrete. Segmentation of capillary pores, and therefore concrete durability, can be improved not only by reducing the w/c ratio, but also by increasing the degree of hydration (a) as shown by the equation [1.0]. Table 2 shows the water/cement ratio and the curing

time required to obtain this condition (1). For instance, if the w/c ratio is 0.60 a 6-month curing time is needed, i.e. concrete must be kept in damp ambient for 6 months before the impermeability of concrete is obtained. On the other hand, with a w/c ratio of 0.35 only 1-day curing time is sufficient to obtain an impermeable concrete (Table 2).

Table 2. Time required to produce maturity at which capillary pores become segmented (1)

w/c ratio	Time required
0.35	1 day (2)
0.40	3 days
0.45	7 days
0.50	2 weeks
0.60	6 months
0.70	1 year
> 0.70	impossible

To increase the degree of hydration, concrete must be kept damp the longest possible time. Table 2 shows the curing time needed to ensure concrete watertightness. In theory, the best curing is to keep concrete damp, by ponding it or covering with wet hessian. In practice, to reduce the curing time within acceptable time limits, a low w/c ratio should be adopted. Then structures could also be protected by applying curing agents, that is, water retentive membranes which are sprayed onto concrete as soon as it has been demoulded.

It is worth underlining the importance of an adequate curing, especially in dry climates and for those structures which, subjected to steam curing, are warm and therefore prone to a higher water evaporation. An adequate curing is required not only to ensure watertightness of concrete structures, but also to avoid concrete - prematurely exposed to air - to dry up, thus causing exaggerated shrinkage and, consequently, dangerous cracks, which lead, in turn, to the corrosion of reinforcement.

3. The influence of water reducers and air-entraining agents on concrete durability

Water reducers are chemical admixtures which are able to reduce the w/c ratio at a given workability or to increase workability at a given w/c ratio. Water reducers include plasticizers and the more effective superplasticizers. By using superplasticizers, both reduction in w/c ratio and increase in workability can also be

obtained, so that flowing concretes (slump higher than 200 mm) with a w/c ratio as low as 0.40 or even 0.35, may be produced. These mixes allow highly reliable pours to be carried out even in very difficult operating conditions (thin sections, highly congested reinforcements, low quality workmanship, poor compaction).

Moreover, by using water reducing admixtures, the curing time before the exposure to aggressive agents may be significantly reduced, since by reducing the w/c ratio a shorter curing time is required to ensure segmented capillary pores and therefore concrete watertightness (Table 2).

Consequently, as a matter of fact superplasticizers are able to affect positively all the parameters controlling durability, since: a) they reduce the w/c ratio; b) they increase the workability of the fresh mix, and c) they even reduce the curing time required to attain a certain degree of hydration (*a*).

Many papers and some symposia (3-5) have been devoted to the beneficial effect of superplasticizers on the concrete durability. In the present report the author of the present paper will focus the discussion only to some relatively recent subjects concerning the severe aggression of sulphate and chloride. Moreover, the effect of air-entraining agents on concrete frost resistance will be critically examined.

3.1 Sulphate attack causing thaumasite

Thaumasite is formed by the reaction of sulphate with cement paste particularly at low temperature (0°C to 5°C) and high relative humidities (90 to 100%). Even if its rough chemical formula ($\text{CaSO}_4 \cdot \text{CaCO}_3 \cdot \text{CaSiO}_3 \cdot 15\text{H}_2\text{O}$) appears to be very different from that of ettringite ($\text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), thaumasite crystal structure $\{\text{Ca}_6[\text{Si}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\} \cdot [(\text{SO}_4)_2(\text{CO}_3)_2]$, is an isostructural phase with that of ettringite, $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\} \cdot [(\text{SO}_4)_3]_2$, so that thaumasite hardly ever can be distinguished from ettringite by X-ray diffraction analysis. This means that in the past time many of the deterioration mechanisms ascribed to ettringite formation could have been really due to thaumasite production.

Formation of both ettringite and thaumasite is accompanied by swelling. However, the effect of swelling is quite different: in general, ettringite formation causes cracks whereas thaumasite formation makes the cement paste so weak that hardened concrete is transformed into a pulpy mass (Fig. 1). Therefore sulphate attack causing thaumasite formation appears to be much more aggressive and dangerous than that causing ettringite formation.

It has been generally assumed that, for durable concrete able to resist the sulphate attack, two important factors should be taken into account: a) a low w/c ratio; b) the choice of a low C_3A portland or pozzolanic cement to reduce the available aluminium content required to produce ettringite. However, thaumasite does not contain aluminium ions so that it can be formed even if a zero C_3A cement is used: this means that to hinder thaumasite production a low w/c ratio becomes much more important.

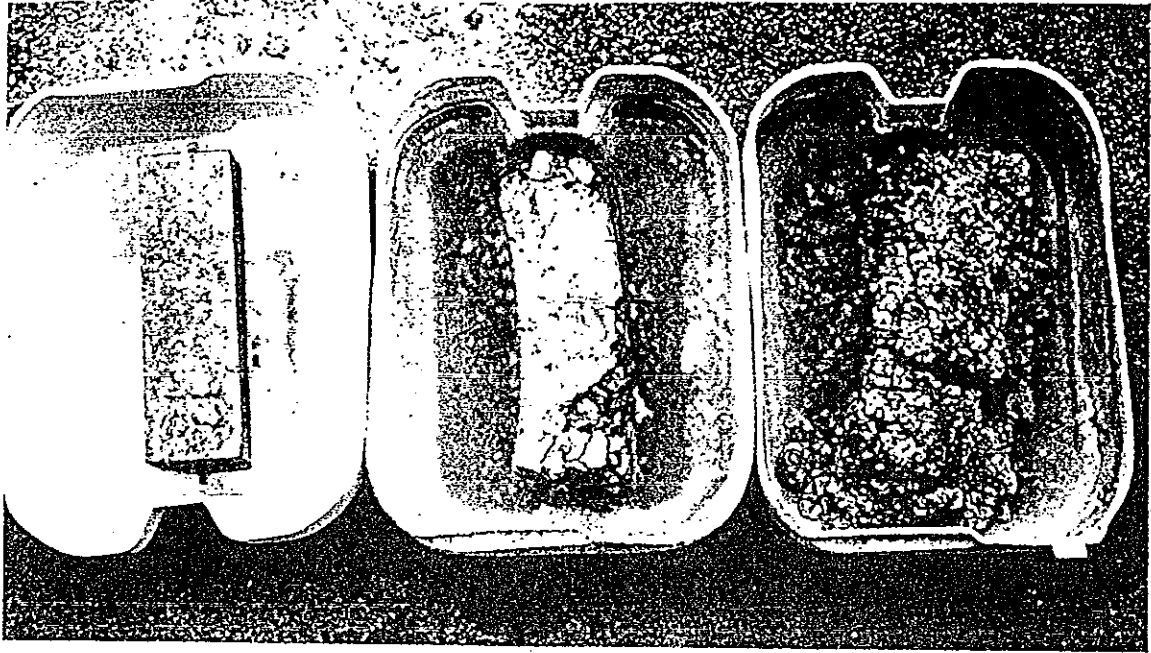


Fig. 1

View of concrete specimens deteriorated by sulphate attack to a different extent by thaumasite formation: on the left the specimen before exposure to sulphate attack; in the middle the damaged specimen with cracks and visible deformation; on the right the specimen fully destroyed by thaumasite formation.

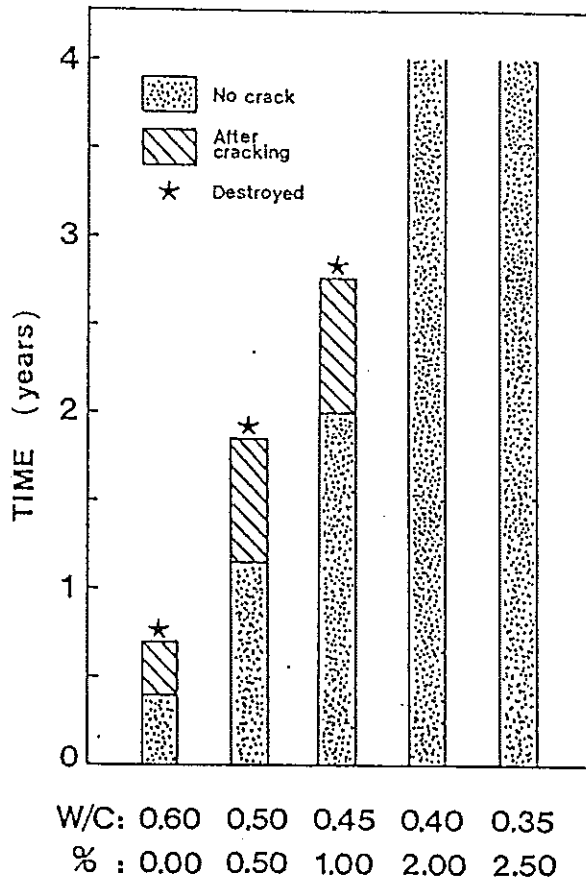


Fig. 2

Sulphate attack: time of cracks appearance and full deterioration as a function of concrete composition. Specimens were immersed at 5°C in a 10% MgSO₄ aqueous solution. The percentage is referred to superplasticizer by weight of cement.

Portland cement concrete specimens with different w/c ratio have been kept under 10% $MgSO_4$ water solution at $5^\circ C$ in order to create the most favourable conditions to produce thaumasite. Figure 2 shows the time of cracks appearance and full deterioration as indicated by specimens in Fig. 1. One can see that only with a w/c ratio lower than 0.40 highly durable concretes, able to resist such a severe attack, may be produced. This means that superplasticizer dosages of 2-3%, and therefore higher than the usual value (1% by weight of cement), should be utilized.

3.2 Chloride attack (from $CaCl_2$) destroying concrete

It is well known that chloride salts penetrate concrete cover and then can promote corrosion of rebars. This can occur in reinforced concrete structures exposed to deicing agents ($NaCl$ or $CaCl_2$) or sea water. By reducing the w/c ratio by using superplasticizers, chloride diffusion through the concrete cover can be significantly reduced and steel corrosion in reinforced concrete structures can be avoided (6).

Till to ten years ago, chloride has been considered to be an aggressive agent only for steel reinforcement and not for concrete itself. In 1975 Chatterji (7) discovered that chloride, in form of 30% $CaCl_2$ aqueous solution, can also attack concrete by destroying it very quickly provided that the temperature is lower than $20^\circ C$, preferably $5^\circ C$. Monosi, Alverà and Collepari (8) have found that the "Chatterji effect" occurs even with 10% $CaCl_2$ aqueous solution and at temperatures higher than $20^\circ C$, although lower temperatures, such as $5^\circ C$, create the most severe conditions to the $CaCl_2$ attack.

According the opinion of the author of the present report, such a type of concrete damage really occurs after the treatment of concrete structures with $CaCl_2$ in winter time, even if is not as severe as in a laboratory test due to the lack of a continuous presence of a concentrated $CaCl_2$ aqueous solution. Moreover, the action of $CaCl_2$ on concrete has been masked, for a long period of time, by another deterioration mechanism, that is the frost action. Very deep cracks appear in 2-3 weeks and concrete is destroyed in few months when it is continuously exposed to a 30% $CaCl_2$ aqueous solution at $5^\circ C$ (Fig. 3), even if it has been manufactured with superplasticizers (1-2%) and with w/c ratio as low as 0.40-0.45. Only the combined addition of superplasticizer (2%) and a very active pozzolan, such as silica fume (15% by weight of cement), can allow to produce durable concrete resisting the very severe $CaCl_2$ attack (Fig. 4).

As far as the type of chemical product causing the "Chatterji effect" is concerned Monosi and Collepari have found (9) that $3CaO \cdot CaCl_2 \cdot 15H_2O$ is the main responsible of the deterioration mechanism. The product forms by reaction of $CaCl_2$ with $Ca(OH)_2$ which is present in the cement paste and this could also explain why, besides superplasticizer, silica fume is required to dramatically reduce the available amount of free lime and produce $CaCl_2$ durable concrete. Since $3CaO \cdot CaCl_2 \cdot 15H_2O$ is stable only in wet cement pastes (8), this product has not been found by other researchers probably for the drying treatment of the ground cement paste before the X-ray diffraction analysis.

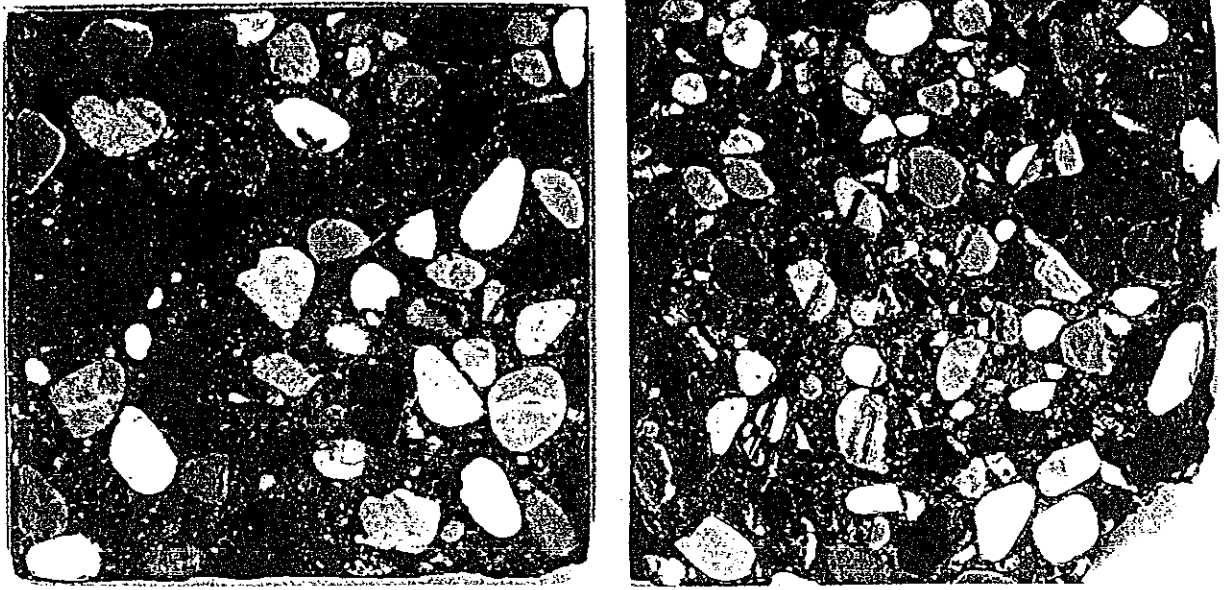


Fig. 3
Concrete specimen before and after the CaCl_2 attack.

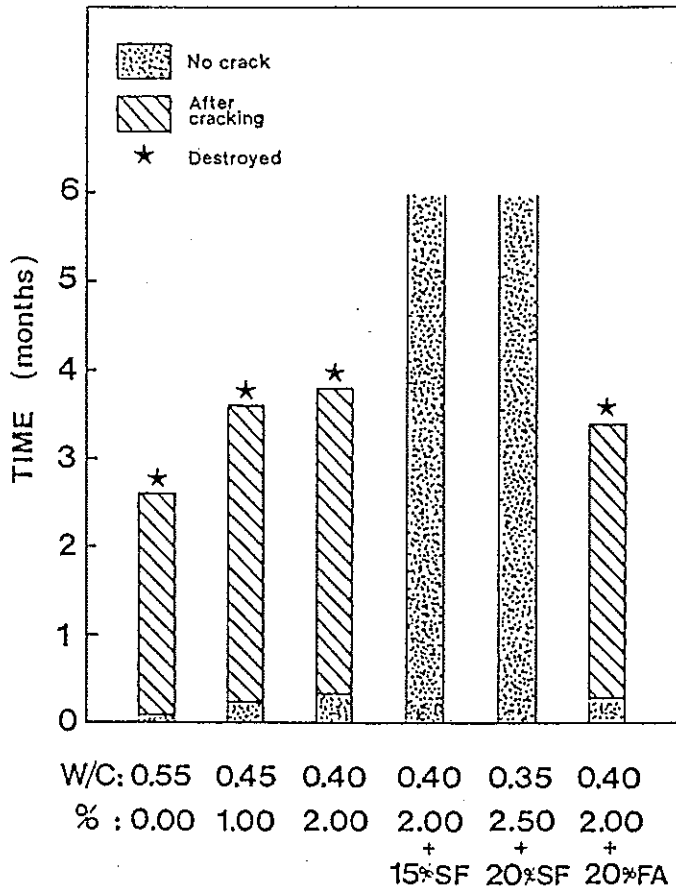


Fig. 4
Calcium chloride attack: time of cracks appearance and full deterioration as a function of concrete composition. Specimens were immersed at 5°C in a 30% CaCl_2 aqueous solution. The percentage values indicate the dosages of superplasticizer. S.F. = silica fume; F.A. = fly ash.

3.3 Alkali attack (from NaCl) accelerating alkali-aggregate reaction

It is well known that concrete containing both reactive aggregates (particularly amorphous silica) and alkali rich cement ($\text{Na}_2\text{O} \geq 0.6\%$) may deteriorate (expansion, cracking, etc.) in ambient with high R.H.

The rate and the extent of the alkali-aggregate reaction depends on many factors, such as the alkali content of cement, the amount of reactive aggregates, the degree of aggregate reactivity, the hygrothermal conditions, etc. Chatterji (10) found that exposure of concrete to a 10% NaCl aqueous solution accelerates the alkali-aggregate reaction, so that cracks appear much earlier. The author of the present paper has found that concretes containing not very reactive aggregate (according to the ASTM C227) and which are able to perform quite well for a long time even in combination with an alkali rich cement, become very reactive when exposed to a 10% NaCl aqueous solution (Fig. 5).

This means that aggregates devoted to concrete structures, which should be exposed to deicing agents (NaCl), should be tested in a more severe and realistic way, i.e. by evaluating the alkali-aggregate reaction of concrete specimens by keeping them under a NaCl aqueous solution.

The addition of superplasticizer alone (1 to 2%) does not substantially improve the durability performance of the alkali-aggregate reaction when tested in the presence of NaCl (Fig. 6). Additions of fly ash or silica fume (10%) plus superplasticizer (1 to 2%), allow concrete specimens to perform very well in the presence of NaCl (Fig. 7).

3.4 Freezing and thawing

It is well known that freezing-thawing cycles can attack very severely a certain type of porous materials such as concrete. Even in a superplasticized concrete with reduced capillary porosity, the frost resistance is not satisfactory, although is better than in a plain concrete mix. Up to now, the only way we know to manufacture frost resistant concrete is to entrain a certain volume of air bubbles (Fig. 8). Since the air-entrainment reduces strength, a combined addition of an air-entraining agent and a plasticizer or superplasticizer allow concrete to become frost resistant without losing initial strength or modulus of elasticity; in other words plasticizers, and even more superplasticizers, compensate the strength loss, caused by the air entrainment, by reducing the water/cement ratio.

On the basis of the above assumptions one could think that concrete frost resistance is not a problem when an air entraining agent is used. But this is not completely true. To a certain extent concrete frost resistance *in practice* is still a problem, even in the presence of an air entraining agent, because of the following reasons:

- 1) the minimum air volume required to guarantee concrete frost resistance depends on the concrete mix proportion and in particular on the coarse aggregate

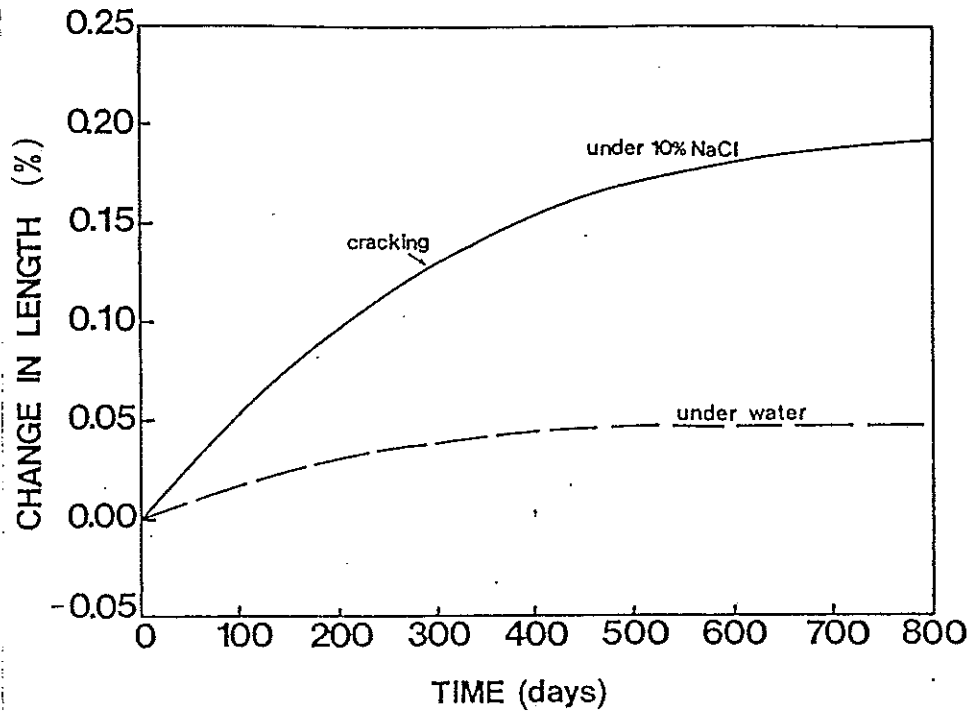


Fig. 5

Sodium chloride attack: expansion of plain concrete specimens ($w/c = 0.6$) kept under water or 10% NaCl aqueous solution. The aggregates were considered to be "potentially" reactive according by the ASTM C227.

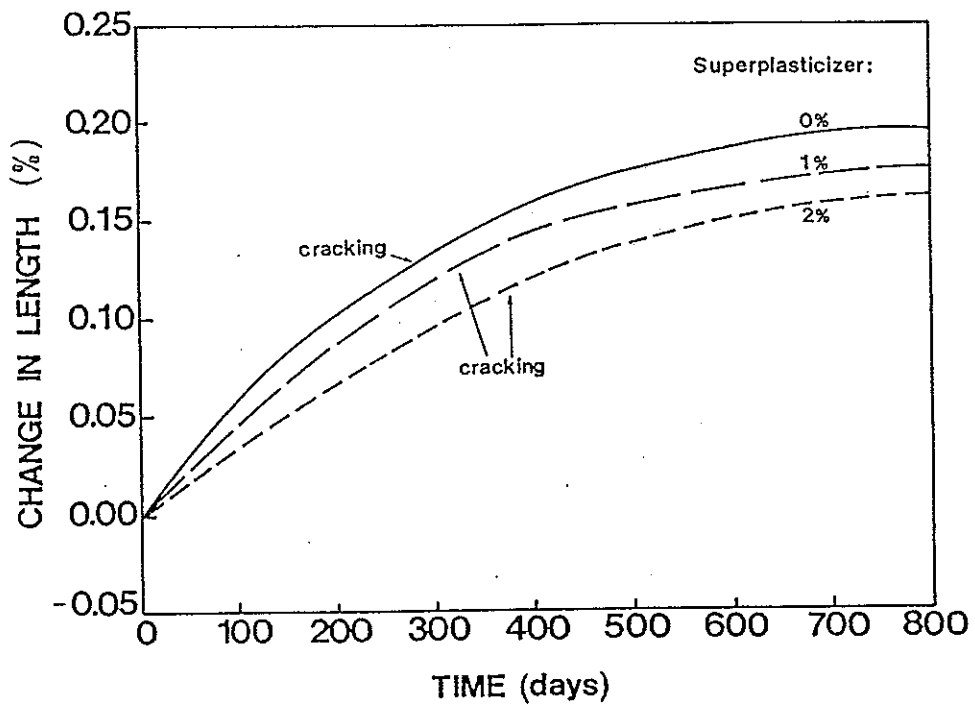


Fig. 6

Expansion of plain and superplasticized concretes caused by 10% NaCl. The aggregates were considered to be "potentially" reactive according the ASTM C227.

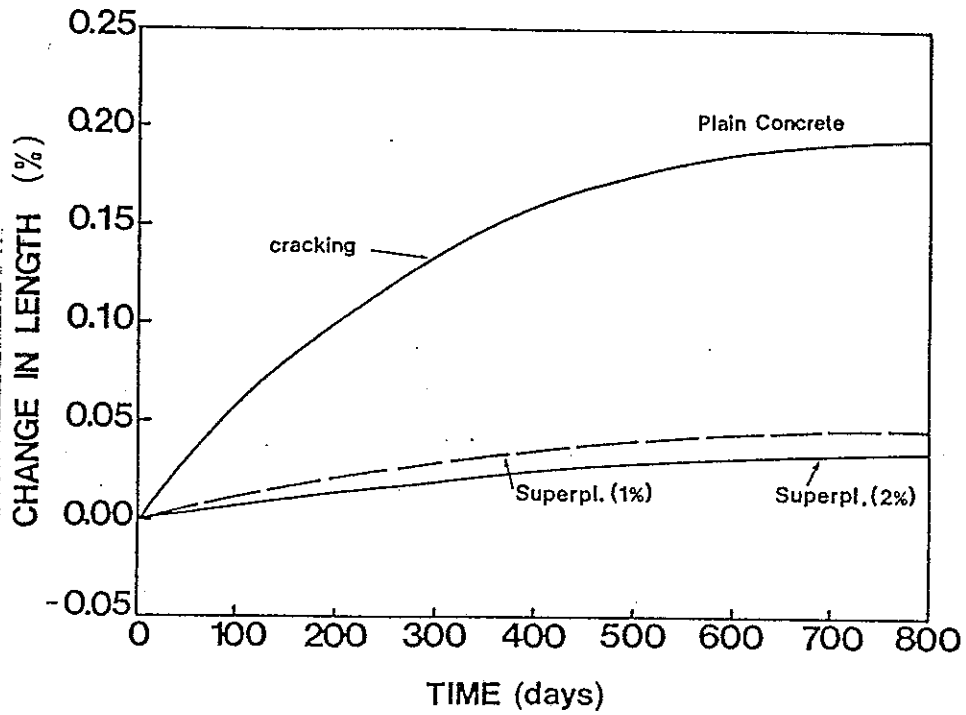


Fig. 7

Expansion of concrete with or without fly ash (F.A.) or silica fume (S.F.), plus superplasticizer. The aggregates were considered to be "potentially" reactive according the ASTM C227.

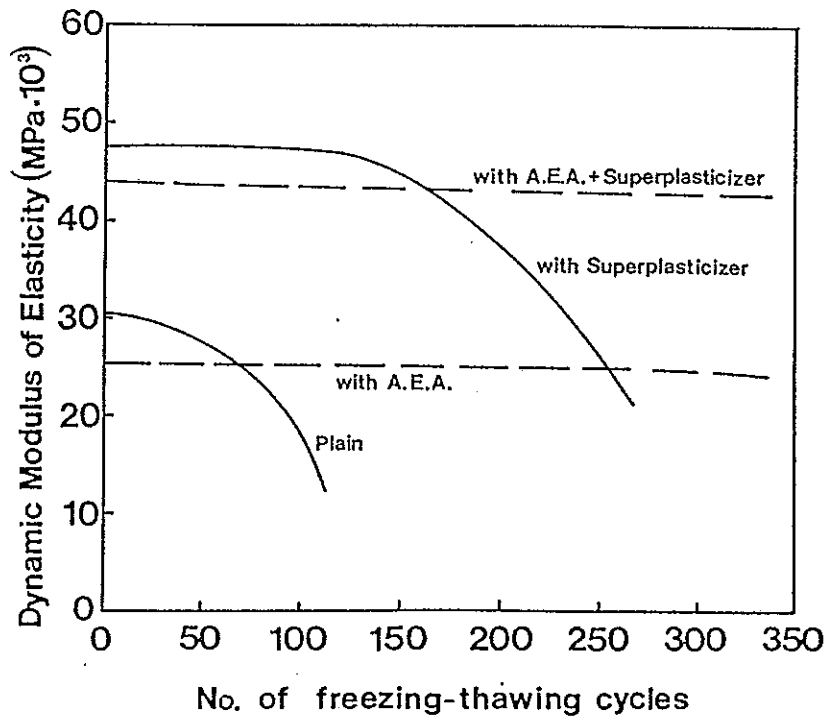


Fig. 8

Modulus of elasticity as a function of freezing-thawing cycles: effect of superplasticizer and air-entraining agent (A.E.A.) on concrete frost resistance.

maximum size (c.a.m.s.): the higher the c.a.m.s., the lower the required minimum air volume; if the air volume is higher than the required minimum value, the strength loss caused by air bubbles becomes higher than the scheduled one; on the other hand, if the air volume is lower than the required minimum value, the frost resistance is lost; any change in the concrete mix proportions and in particular in the c.a.m.s. value should require a proper adjustment in the volume of entrained air: *this is easy to do in a laboratory, but is very difficult to do on a job site;*

2) even if we were able to keep constant the concrete mix proportion and the c.a.m.s., the volume of entrained air into the concrete at the batching plant may significantly deviate from the scheduled one, because the entrained air volume strongly depends on the concrete slump, revolution rate of concrete mixer, amount of concrete, temperature, sand fineness, etc., so that *is substantially impossible in practice to keep constant air volume from one batch to another;*

3) even if we were able to keep constant the air volume at the batching plant, we must take into account that for the concrete frost resistance, is very important not the air volume at the batching plant, but the air volume in the *placed* concrete: after mixing and before placing concrete, there are two processes which significantly affect the air volume: transportation and compaction; the longer the transportation time, the higher the air volume lost during the transportation; the higher the temperature, the higher the air volume lost during the transportation; pumping and spraying are processes which furtherly reduce the air volume into the concrete; compaction is even more important in reducing the air volume: longer and more effective is the compaction, the lower is the air volume kept in the placed concrete. Therefore *it is impossible to keep constant air volume in all placed concrete structures.*

By taking into account all these factors we could conclude that it is easy to say that air entrained concrete is frost resistant, but is very difficult to do it in practice. In other words, air entrainment is only a theoretical solution of the concrete frost resistance problem: it works quite well for concrete specimens manufactured in a laboratory, but it does not work in practice to make concrete structures (such as bridge decks, slabs, etc.) which should be *definitely* frost resistant.

To support such a statement is sufficient to think about the difference in the frost resistance behaviour of concrete structures in USA and Europe. This difference is negligible, even if concrete people in Europe do not use air entraining agents to the same extent as the Americans do. In other words bridge decks deteriorate in USA as well as in Europe.

Up to now, the use of air entraining agents has been accepted as the best solution available for the concrete frost resistance problem, even if it has not been satisfactory in practice. Now is time to look for a better solution. This means to find a solution which definitely works both in a laboratory and at a job site.

4. Conclusions

Since a long time it has been experienced that water reducers (and particularly superplasticizers) and air-entraining agents may be used very advantageously to improve concrete durability. However, some specific chemical attacks on concrete, such as those caused by sulphate in cold weather or by CaCl_2 and NaCl , need an increase in the superplasticizer dosage or a combined addition with silica fume and fly ash, respectively.

Air-entraining agents allow the production of frost resistant concrete specimens, provided some requirements are met. Due to the difficulties found *in practice* to meet such requirements at the job site, intensive research work is necessary in the future in order to obtain frost resistant concrete structures, which should be as durable as laboratory produced specimens are.

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