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ABSTRACTS
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PROGRESS IN CONCRETE SCIENCE AND TECHNOLOGY FOR MARITIME WORKS

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ABSTRACT

Water reducers, and in particular superplasticizers, may be advantegeously used to improve concrete durability against many chemical attacks including ions such as sulphate and chloride in sea water. A combined addition of superplasticizer and mineral additions such as fly ash or silica fume allow the production of even more durable concretes. Air-entraining agent are used to manufacture frost resistant concrete.

1. Causes of concrete deterioration

The durability of concrete is the ability of the material to last and resist the aggressive action of the environment. The reason 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 environment and choosing a level of adequate durability for the concrete.

The choise 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 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 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. For maritime works the aggressive agents include ions of sea water in addition to freezing thawing cycles for areas exposed to cold climatic environments. Ions of sea water which can damage reinforced concrete structures are: sodium ions for reactive aggregates, sulphate ions for cement paste and chloride ions for the reinforcing steel bars.

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 discontinuos porosity which does not allow agents to permeate the material.

Table 1. - Main causes of concrete deterioration

Due to the material	Due to the environment
Inadequate Concrete Composition (water/cement ratio, aggregate/cement ratio and air void system)	*Chemical causes:* - sulphate; - carbon dioxide; - inorganic acids (if pH is below 5, concrete requires a portective coat); - alkali; - chloride.
Inadequate Workability of concrete during placing	
Inadequate Curing of concrete after demoulding	*Physical causes:* - freezing and thawing; - drying process (shrinkage); - high temperatures.
	Mechanical causes: - abrasion; - erosion; - cavitation.

Concrete basically has types of voids wich are responsible for the permeability of the material: capillary pores (with a diameter varying between 0.01 and 10 μm) in the cement paste wich coats aggregates, and macrovoids, having a much greater size (0.1 to 10 mm), 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 (α) that reacted with water. The lower the water/cement ratio, the lower the distance among cement grains will be and less porous will be microstructure of the hydration products. On the other hand, the higher the degree of hydration (α), the higher the volume of the cement hydration products will be and, therefore, the lower the capillary porosity will be. The equation (1) 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 (α).

$$V_p = 100\, w/c - 36.15\,\alpha \qquad (1)$$

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) a decreased capillary porosity can be obtained by lowering the w/c ratio and by increasing the degree of cement hydration (α), 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 previous section, would simply become theoretical exercises. In fact, taking into consideration job-site operating condition, 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 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 (α) as shown by the equation (1). Table 2 shows the water/cement ratio and curing time required to obtain this condition [1]. For instance, if the *w/c* ratio is 0.60 a 6-month curing time is neeeded, i. e. concrete must 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 time 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 wich 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, wich 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 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 (α).

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 autors 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° to 5 °C) and high relative humidities (90 to 100%). Even if its rough chemical formula ($CaSO_4 \cdot CaCO_3 \cdot CaSiO_3 \cdot 15\ H_2O$) appears to be very different from that of ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$), thaumasite crystal structure ($Ca_6[Si(OH)_6]_2 \cdot 24H_2O) \cdot [(SO_4)_2 (CO_3)_2]$ is an isostructural phase with that of ettringite, ($Ca_6[Si(OH)_6]_2 \cdot 24H_2O) \cdot [(SO_4)_3[2H_2O]$, 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 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.

Portland cement concrete specimens with different *w/c* ratio have been kept under 10% $MgSO_4$ water solution at 5 °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 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 ($Na_2O > 0.6\%$) 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 [6] found that exposure of concrete to a 10% NaCl aqueous solution accelerates the alkali-aggregate reaction, so that cracks appear much earlier. The authors of the present paper have found that concretes containing not very reactive aggregate (according to the ASTM C227) and wich 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. 3).

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. 4). 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. 5).

3.3 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. 6). Since the air-entrainment reduces strength, a combined addition of an air-entraining agent and a plasticizer or superplasticizer allows concrete to become frost resistant without loosing 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 resistence 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 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 adjustement in the volume of entrained air: *this is easy to do in 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 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: the 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 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 wich definitely works both in a laboratory and at a job site.

4. Conclusions

Since a long time it has beeen experienced that water reducers (and particularly superplasticizers) and air-entraining agents may be used very advantageously to improve concrete durability. A combined addition of superplasticizer with silica fume furtherly improves concrete durability.

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 conccrete structures, which should be as durable as laboratory produced specimens are.

5. References

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[6] S. Chatterji, *Cement and Concrete Research*, 8, 647-650, (1978).

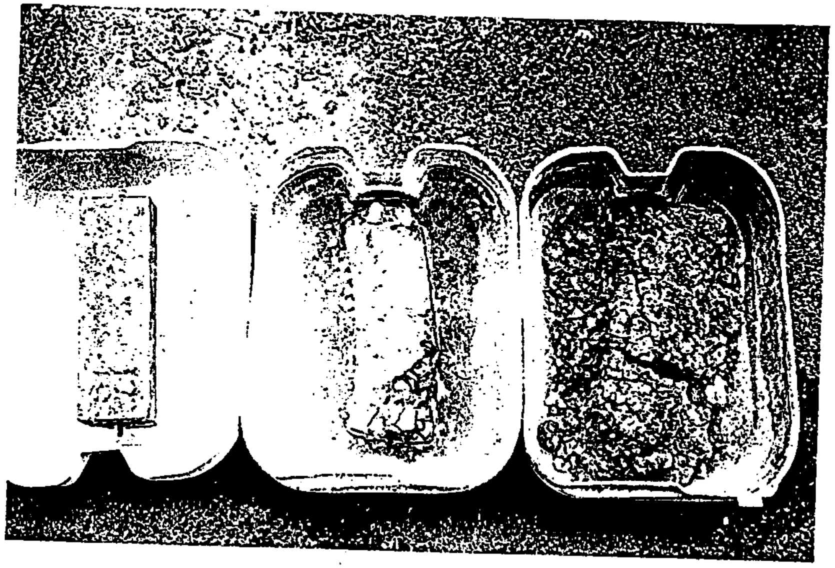

Fig. 1 - View of concrete specimens deteriorated by sulphate attack to a different extent by thaumasite formation: on the left the specimen before exposure to sulphate attack; in the middle the damaged specimen with cracks andvisible deformation; on the right the specimen fully destroyed thaumasite formation.

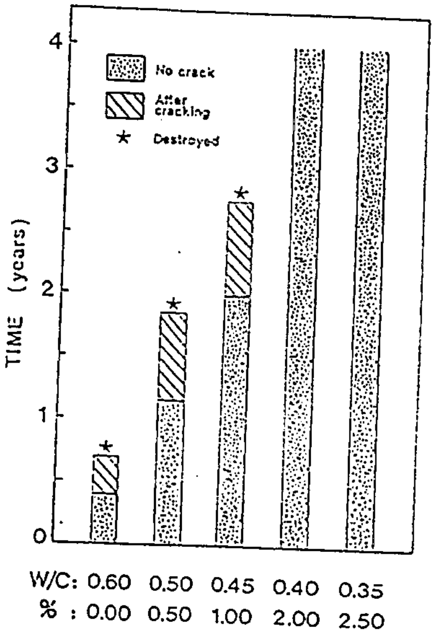

Fig. 2 -
Sulphate attack: time of cracks appearance and full deterioration as a function of concrete composition. Specimens were immersed at 5 °C in a 10% $MgSO_4$ aqueous solution. The percentage is referred to superplasticizer by weight of cement.

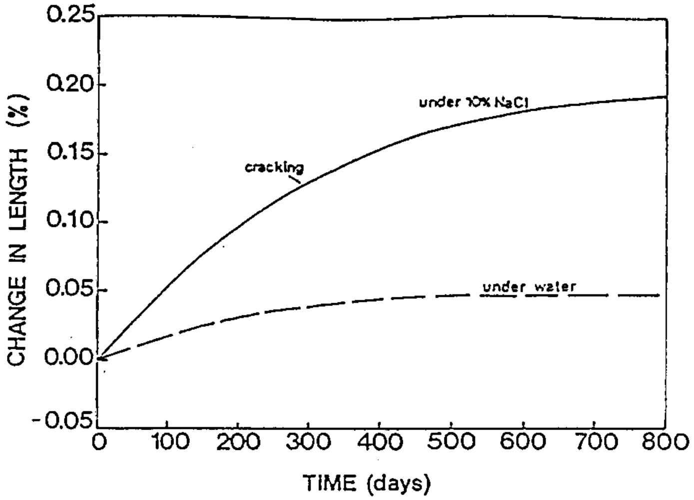

Fig. 3 - Sodium chloride attack: espansion of plain concrete specimens (w/c = 0.6) Kept under water or 10% NaCl aqueous solution. The aggregates were considered to be "potentially" reactive according by the ASTM C227

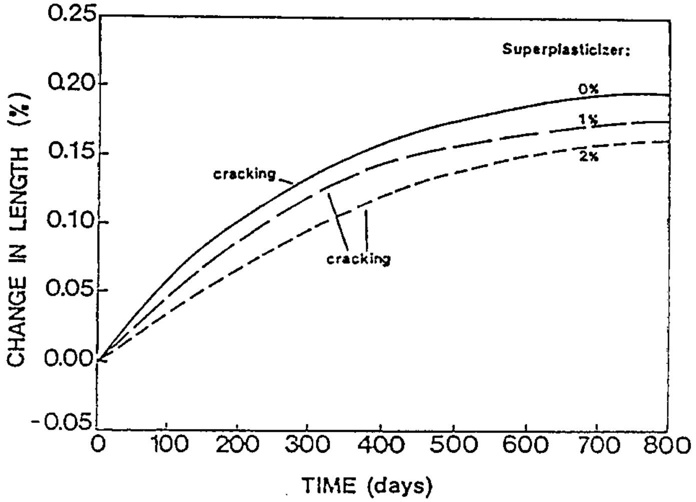

Fig. 4 - Expansion of plain and superplasticized concretes caused by 10% NaCl. The aggregates were considered to be "potentially" reactive according by the ASTM C227

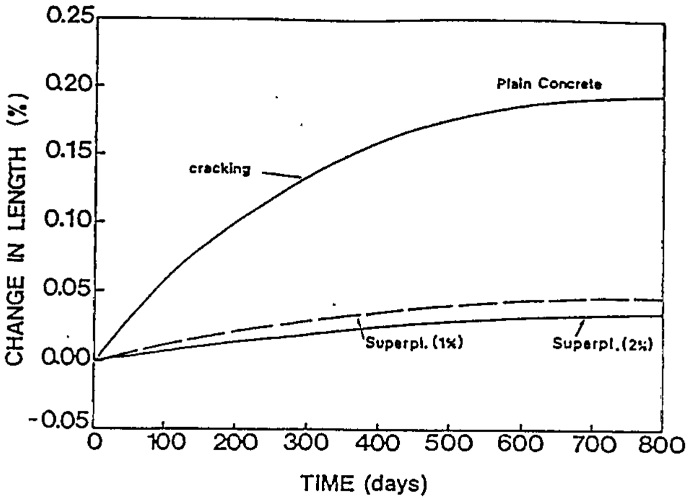

Fig. 5 - Expansion of concrete with or without fly ash (F.A.) or silica fume (S.F.), plus superplasticizer. The aggregates were considered to be "potentially" reactive according the ASTM C227

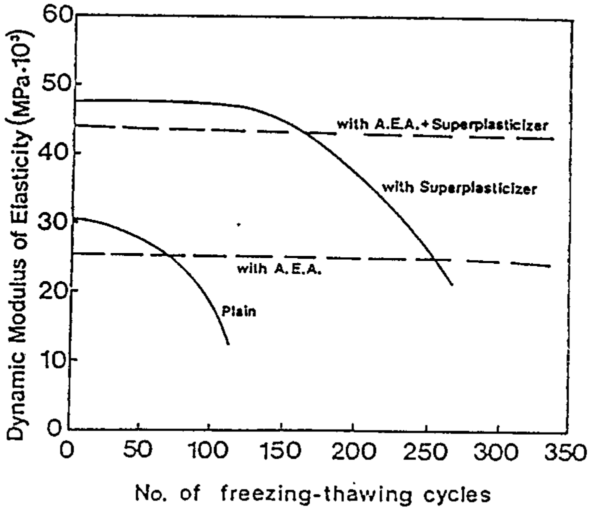

Fig. 6 - Modulus of elasticity as a function of freezing-thawing cycles: effect of superplasticizer and air-entraining agent (A.E.A.) on concrete frost resistance.