NEW GENERATION OF SUPERPLASTICIZERS FOR HIGH PERFORMANCE CONCRETE (HPC)

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ABSTRACT

Admixtures have been used in the concrete industry for many decades. They were usually by-products of particular primary material production that eventually found an application as a concrete admixture. Since its composition and hence its properties can only be modified within narrow limits, its performance in concrete is limited. Specific requests from the concrete industry created a need to develop polymers with the desired performances. Requests for high strength and high performance concrete (HPC) top the list. Design codes have been updated in many countries to provide for the use of concretes with earlier unknown strength and durability performances. The challenge for the construction industry is to design, manufacture and to deliver such concretes with locally available materials. These concretes should be easily placable, i.e. they must maintain workability up to the finishing stage.

A new generation of superplasticizers, based on polycarboxylate ether polymers (CE) which allow for a reduction of water content of up to 40 % and at the same time give an extended slump retention will make the production of such high performance concretes a realistic task.

KEYWORDS

High performance and high strength concrete, durability, water/cement ratio, slump loss, extended slump retention, concrete workability, mixing water reduction.

INTRODUCTION

Concrete, in some form or the other, has been in use for more than 6000 years. Babylonians and Assyrians first used a mixture of clay, lime and water. Later civilizations developed these initial mixes. In 1824, Joseph Aspdin "invented" the Portland Cement (PC). But it was only when concrete has been brought into the laboratory, that it became ***the*** building material of this century.

The correlation between the strength of a concrete to its water content : Abram and Powers' (1964) studies linking the porosity, the water cement ratio and degree of hydration of the cement to its strength, greatly improved knowledge of the concrete and set the basis for its wide spread use.

In the past the main objective in the production of concrete was to achieve "High Strength Quality". Today, the name of the game is "High Performance Concrete" (HPC). There is a distinct difference between the two. The difference is durability ! "High strength" alone does not necessarily stand for durability.
Durability - a long life span - is today a basic requirement of concrete.

DURABILITY OF CONCRETE

The quality - or durability - of concrete is not only a function of its compressive strength but as much one of its porosity (impermeability). The following Figure 1 illustrates the factors influencing the quality of concrete.

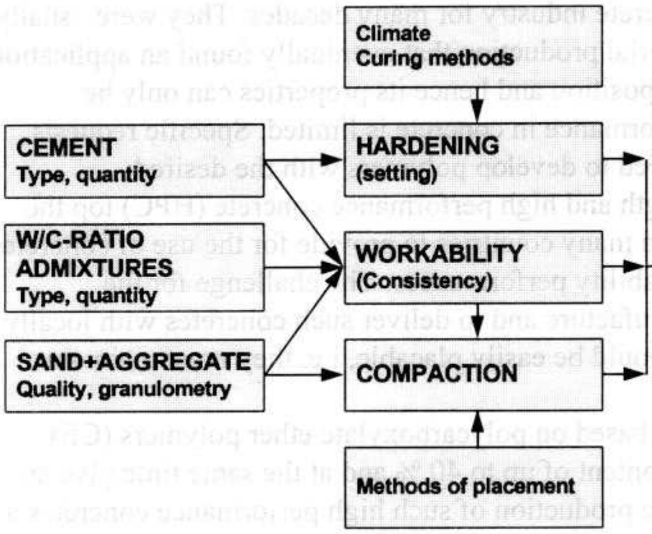


Figure 1. Factors influencing the concrete quality

As one can see, the porosity of hardened concrete is largely influenced by the water/ cement ratio (w/c) and the placement technique.

We know from Powers equation Eq (1)

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

that at identical degree of cement hydration α : Powers (1964); Oberholster (1986) and decreasing w/c, the result is a reduction in capillary porosity of the hardened cement paste (Vp).
Figure 2 illustrates the influence of the w/c ratio on the porosity of concrete.

The lower the porosity of a concrete the better is its impermeability. High impermeability makes a concrete also less sensitive to the ingress of aggressive agents such as carbon dioxide, chlorides, sulphate ions, etc.

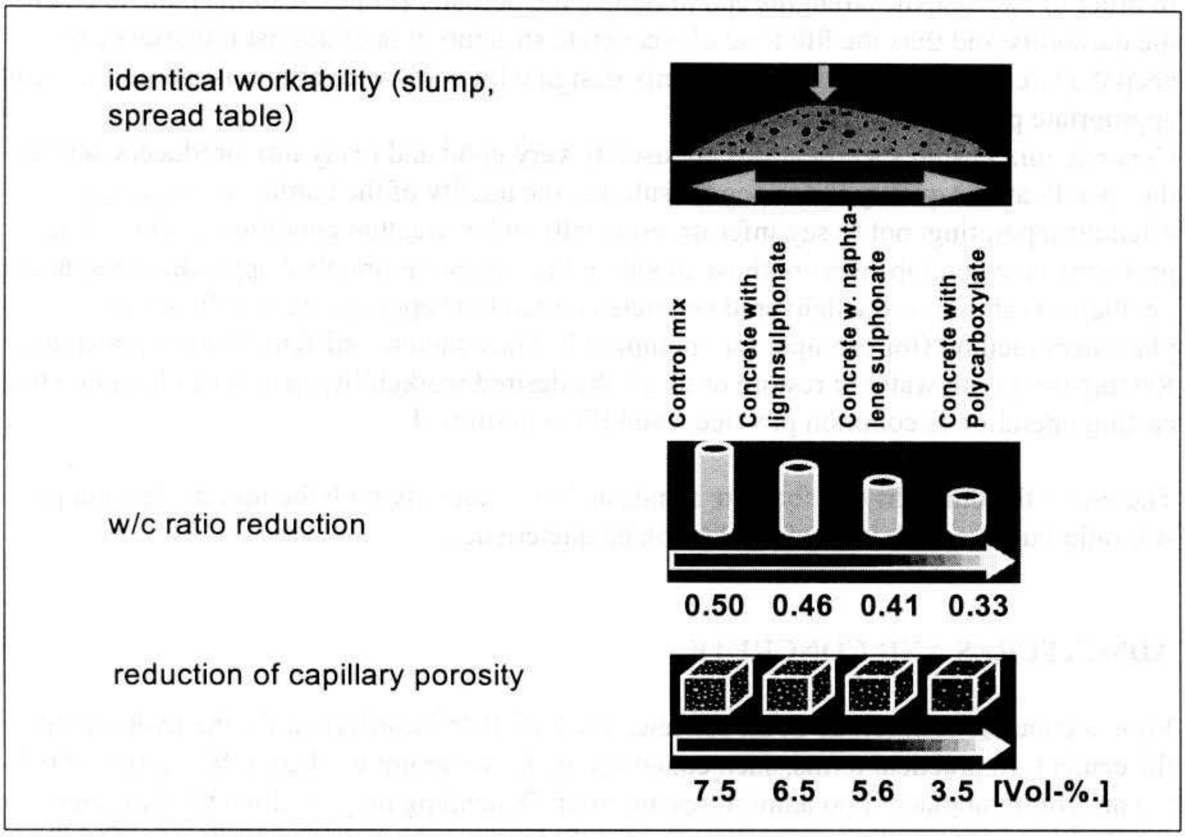


Figure 2. Correlation between w/c and porosity

Knowing the influence of the w/c ratio on the capillary porosity, it does not come as a surprise that the w/c ratio has also a great influence on concrete's the strength. The correlation between w/c and strength is shown in Figure 3.

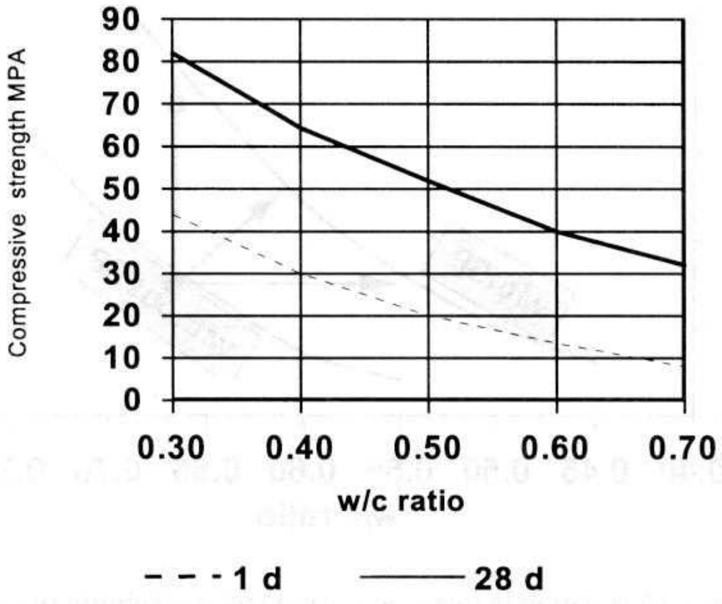


Figure 3. Correlation between w/c and compressive strength

In order to increase the strengths and to reduce the porosity (impermeability), i.e. to extend the durability and thus the life time of a concrete structure it is of utmost importance to keep the w/c as low as possible. Good mix design with a low w/c ratio must go in line with appropriate placing on the job site.
Concrete mix design specifications are usually very good and ready mix producers deliver the specifications quality but the end result, i.e. the quality of the hardened concrete is often disappointing, not to say inferior, especially in hot weather conditions. Why ? The problems faced on job sites are those of slump loss or/and impractical application methods, i.e. the workability of the delivered concrete is often not "appropriate" to allow easy placement method (for example for "pumping"). The concrete "stiffens" during transport. Retempering with water to restore or to get the desired workability in order to facilitate the casting operation is common practice, even if not permitted.

Therefore, the durability of concrete stands and falls not only with the mix design and its w/c ratio but also with its slump retention characteristics.

ADMIXTURES AND CONCRETE

From a concrete technology point of view, a w/c of 0.25 is sufficient for the hydration of the cement. In practical terms, such concretes are however not workable. W/c ratios of 0.5 - 0.7 are common place if no admixtures are used. Depending on granulometry and fines (sand, filler) content, the workability even of these mixes are not necessarily yet "fluid". Segregation and bleeding are other problems facing in relation to high water contents. Good concrete without the use of admixtures is difficult to place and requires intensive and time consuming vibration for full compaction. In order to reduce the water content and for improving workability, water reducing admixtures are essential. Figure 4 shows the correlation w/c ratio and concrete workability.

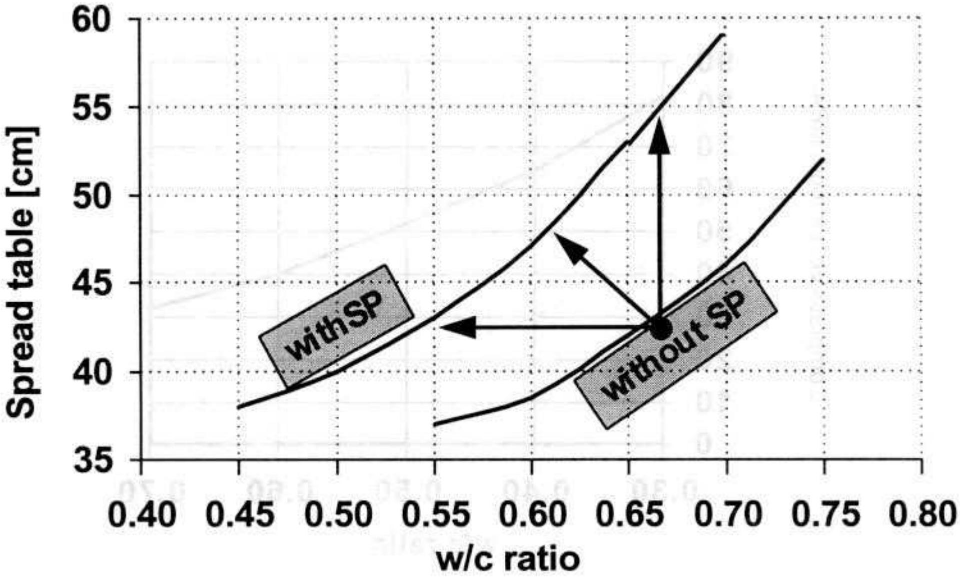


Figure 4. Correlation between w/c/ ratio and workability of concrete (SP = Superplasticizer)

The commonly available admixtures with good to high plastisizing effects are :

- Modified ligninsulphonates (MLS)
- Sulphonated melamine condensates (SMF)
- Sulphonated naphthalene condensates (SNF)
- Polycarboxylic ethers (CE)

Table 1. Typical performances of water reducing admixtures

Family	Typical dosage by cement weight	Water reduction
Modified ligninsulphonates (MLS)	0.2 - 0.8 %	up to 10 %
Melamine sulphonates (SMF)	1.0 - 3.0 %	up to 25 %
Naphthalene sulphonates (SNF)	0.8 - 2.0 %	up to 25 %
Polycarboxylic ethers (CE)	**0.5 - 1.5 %**	**up to 40 %**

Many authors have pointed out that one of the problems related to the use of super-plasticizers is the increasing slump loss related to other factors such as temperature, type of cement, chemical constituents of cement and cement content : Malhotra (1981), Maillvaganem (1978), Pernchio (1978), Hattori (1978).

In order to overcome this problem set retarders are used in combination with super-plastizeres with consequent retardation of the hardening process in early stages.

It is clear, whether the addition of water on the job site nor the hardening retardation due to the addition of retarders are desired either from the consultant's or contractor's point of view.

The introduction of superplasticizers based on polycarboxylic ethers is a big step forward in overcoming the above mentioned shortcomings.

In this paper I would like to introduce to you this latest generation of superplasticizers and the opportunities which they offer to the concrete industry.

MECHANISM OF ACTION OF CE SUPERPLASTICIZERS

The dispersion mechanism of SNF and SMF based superplasticizers in cement paste can be explained in terms of electrostatic repulsion between the cement particles negatively charged by the adsorption of the polymer molecule onto the cement surface, and is measured by the magnitude of zeta potential.

The dispersion mechanism of polycarboxylate based superplasticizers is mainly due to two different types of repulsion forces between the cement particles : electrostatic repulsions due to the presence of the negative charge given by the carboxylic groups and steric repulsion effect due to the main and long chains of the polymers. The electrostatic repulsion force for CE is half of the value measured for SNF superplasticizers and the dispersion is mainly due to the very strong steric repulsion effect : Otha, Sugiyama and Tanaka (1997), Uchikawa, Hanehara and Sawaki (1997).

The chemical structure of polymers present in the new CE superplasticizers consists of a main flexible backbone, containing negatively charged carboxylic groups, and a large number of side chains. Figure 5 illustrates the molecule.

The interaction between the side chains in the CE polymer helps to obtain a shell-type macromolecule that, in basic solutions progressively opens showing a slow release mechanism. This will improve the dispersion and stability of the cement particles thus preventing their flocculation, even when hydration reaction has started. This is shown in Figure 6.

Recently, several papers have been published mainly by Japanese authors : Kinoshita, Sukuki, Soeda and Nawa (1997), Shonaka and Kitagawa (1997) and Otha, Sugiyama and Tanaka (1997) related to the use of polycarboxylate based superplasticizers and many research activities have been carried out in order to understand their superior efficiency as dispersing agents and their potential to retain the dispersing effect for an extended time in hardened cement pastes.

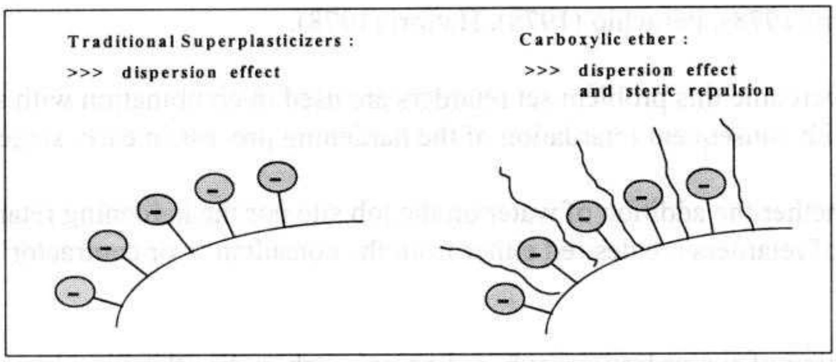


Figure 5. Mechanism of action of superplasticizers molecules

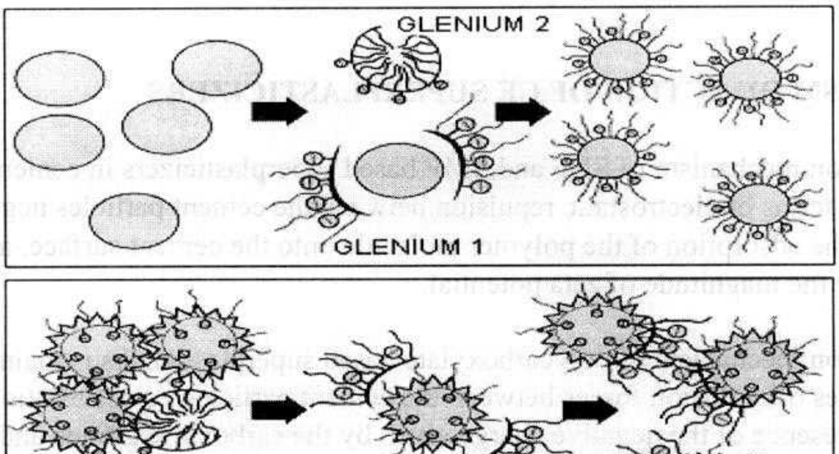


Figure 6. Successive mechanism of action of CE-molecules

EFFECTIVENESS OF CE BASED SUPERPLASTICIZERS

CE admixtures have first been introduced in Japan. Since its introduction in Europe in 1995, extensive laboratory and field test series have been carried out. Tables 2 -7 show the results of a series of field tests done in various countries.

U.A.E. Experiences

Table 2. Lab. trials

Mix Design	1	2	3	4
Cement (kg/m^3)	420	410	400	390
crushed aggregate	1200	1200	1200	1200
Blended dune sand	850	850	850	850
Microsilica (kg/m^3)	-	10	20	30
CE superplasticizer in (% of cw)	1.25	1.40	1.6	1.78
w/c ratio including Microsilica	0.30	0.30	0.30	0.30
Air (%)	0.8	0.6	0.6	0.4
Density (kg/m^3)	2590	2600	2590	2595
BS 5075 Set time initial/final	3:30/4:30	4:00/5:00	4:45/5:45	5:00/6:00
Consistency (Slump - mm) at :				
t = 0 minutes	225	225	225	230
t = 30 minutes	200	215	210	225
t = 60 minutes	65	115	150	225
t = 90 minutes	25	70	110	185
Compressive strength (MPa) at 25 °C				
1 day	44	41	41	40
3 days	73	68	68	64
7 days	81	77	80	83
28 days	95	100	100	107
90 days	101	105	110	111

Table 3. Field trials

Mix Design	1	2	3	4
Cement (kg/m^3)	440	440	440	440
Densified silica fume (kg/m^3)	52	44	49	50
CE superplasticizer in (% of cw)	1.63	1.55	1.64	1.73
water/cement ratio	0.28	0.30	0.28	0.28
Consistency (Slump - mm) at :				
t = 0 minutes	210	210	200	Collapse
t = 30 minutes	190	200	200	Collapse
t = 60 minutes	130	200	190	170
t = 90 minutes	110	200	150	130
Compressive strength (MPa)				
3 days	52	50	62	56
7 days	64	63	78	75
28 days	89	85	102	95

Italian Experiences

Table 4. Concrete with cements type CEM I 52.5 and different types of aggregates

Mix Design	1	2	3	4
Aggregate type	Dolomite	Basalt	Limestone	Limestone
Cement (kg/m^3)	420	420	420	420
Sand (%)	53	42	43	47
Coarse aggregates (%)	47	58	57	53
Densified silica fume (kg/m^3)	50	50	50	50
CE superplasticizer in (% of cw)	1.5	1.5	1.5	1.5
w/c ratio including silica fume	0.33	0.31	0.27	0.31
Air (%)	2.8	2.2	1.9	2.9
Density (kg/m^3)	2450	2550	2550	2425
Consistency (Slump - mm) at :				
t = 0 minutes	230	220	240	220
t = 30 minutes	190	180	220	210
t = 60 minutes	190	170	210	185
t = 90 minutes	170	160	190	185
Compressive strength (MPa) at 20 °C				
1 day	55	56	65	60
7 days	86	91	90	91
28 days	93	112	109	104
90 days	118	122	112	105

Table 5. Concrete with cements type CEM II/A-L 42.5 and different types of aggregates

Mix Design	1	2	3	4
Aggregate type	Dolomite	Basalt	Limestone	Limestone
Cement (kg/m^3)	420	420	420	420
Sand (%)	53	42	43	47
Coarse aggregates (%)	47	58	57	53
Densified silica fume (kg/m^3)	50	50	50	50
CE superplasticizer in (% of cem.w)	1.5	1.5	1.5	1.5
w/c ratio including silica fume	0.31	0.33	0.27	0.32
Air (%)	2.8	1.4	2.4	2.6
Density (kg/m^3)	2475	2575	2500	2450
Consistency (Slump - mm) at :				
t = 0 minutes	220	220	240	210
t = 30 minutes	220	200	220	205
t = 60 minutes	200	190	205	195
t = 90 minutes	190	180	195	180
Compressive strength (MPa) at 20 °C				
1 day	46	44	45	44
7 days	84	81	74	81
28 days	97	102	97	99
90 days	110	182	113	105

Spanish Experiences

Table 6. Concrete with cements type CEM I 52.5

Mix Design	1	2
Cement (kg/m^{3})	450	400
Densified silica fume (kg/m^{3})	45	40
Sand 0 - 5 mm (kg/m^{3})	960	970
Aggregate 3 - 12 mm (kg/m^{3})	850	860
CE superplasticizer in (% of cw)	1.5	1.6
w/c ratio including silica fume	0.32	0.33
Air content (%)	2.9	1.8
Consistency (Slump - mm) at :		
t = 0 minutes	200	180
t = 30 minutes	190	160
t = 60 minutes	180	140
t = 90 minutes	170	120
Compressive strength (MPa) at 20 °C		
1 day	57	71
7 days	85	94
28 days	113	101

Austrian Experiences

Table 7. Concrete with different cements type and aggregates

Mix Design	1	2
Cement type	CEM I 42.5	CEM I 52.5
Cement kg/m^{3}	460	450
Densified silica fume (kg/m^{3})	42	80
Type of aggregate	Limestone	Basalt
Max. size of aggregate	32	22
Total aggregates/sand content (kg/m^{3})	1940	2000
CE superplasticizer in (% of cw)	1.8	1.6
w/c ratio including silica fume	0.28	0.26
Consistency (Spread table flow - cm) at :		
t = 0 minutes	64	60
t = 30 minutes	60	57
t = 60 minutes	58	54
t = 90 minutes	55	55
Compressive strength (MPa) at 20 °C		
1 day	48	51
7 days	73	107
28 days	100	148

HIGH PERFORMANCE CONCRETE

These results illustrate the opportunities offered by CE based superplasticizers. Their influence on some of the key factors (strength, w/c ratio and slump retention) has a great impact on the performance characteristics of concrete. Other parameters which are indirectly positively influenced by the use of CE based superplasticizers - which are also called "advanced superplasticizers" - are those of shrinkage, creep and of elasticity modulus.

We know now about the improvement possibilities of CE based superplasticizers but what is the definition of High Performance Concrete ? To put it frank - the defined parameters seem to be "grey" area :

In the German speaking world the common understanding is that a HPC must
- have a w/c of < 0.40
- contain Silica Fume
- contain a superplasticizer
- be done with normal PC and ordinary quality of sand and aggregate
- have a normal consistency (workability)

Mixes with the above characteristics will result in high strength concrete. Interestingly, the specifications cover only elements of fresh but not performances of hardened concrete. There are no specific strength developments required.

The American Concrete Institute committee has defined HPC in ACI Special Publication SP-140 (Goodspeed) as
"concrete that meets special performance and uniformity requirements that can not always be obtained by using conventional ingredients, normal mixing procedures and typical curing procedures These requirements may include the following enhancements :
- *Ease of placement and consolidation without affecting strength*
- *Long-term mechanical properties*
- *Early high strength*
- *Toughness*
- *Volume stability, and*
- *Longer life in severe environments*

A Strategic Highway Research Programme (SHRP) study reported by Goodspeed (1996) defined HPC as consisting of :
- *maximum w/c ratio of 0.35*
- *minimum durability factor of 80 % (as determined by ASTM C 666, Procedure A and 3)*
- *minimum compressive strength of either a) 21 MPa after 4 hours, b) 34 MPa within 24 h or 69 MPa after 28 days*

The Federal Highway Administration (FHWA) suggests the following grades and parameters for HPC in Table 8 (Goodspeed, 1996).

Table 8. Grades of performance characteristics for high performance structural concrete[1]

Performance characteristic	Standard test method	FHWA HPC performance grade			
		1	2	3	4
Freeze thaw durability rel. dynamic modulus of elasticity after 300 cycles	AASHTO T 161 ASTM C 666 Proc. A	60 - 80 %	< 80 %		
Scaling resistance visual rating of the surface after 50 cycles	ASTM C 672	4,5	2,3	0,1	
Abrasion resistance average depth of wear in mm	ASTM C 944	2- 1	1 - 0,5	< 0.5	
Chloride penetration coulombs	AASHTO T 277 ASTM C 1202	3000 - 2000	2000 - 800	< 800	
Strength compressive strength	AASHTO T 2 ASTM C 39	41 - 55 MPa	55 - 69 MPa	69 - 97 MPa	< 97 MPa
Elasticity modulus of elasticity	ASTM C 469	28 - 40 GPa	40 - 50 GPa	> 50 GPa	
Shrinkage microstrain	ASTM C 157	800 - 600	600 - 400	< 400	
Creep microstrain/pressure unit	ASTM C 512	75 - 60 MPa	60 - 45 MPa	45 - 30 MPa	< 30 MPa

1 *"This table does not represent a comprehensive list of all characteristics that good concrete should exhibit".*

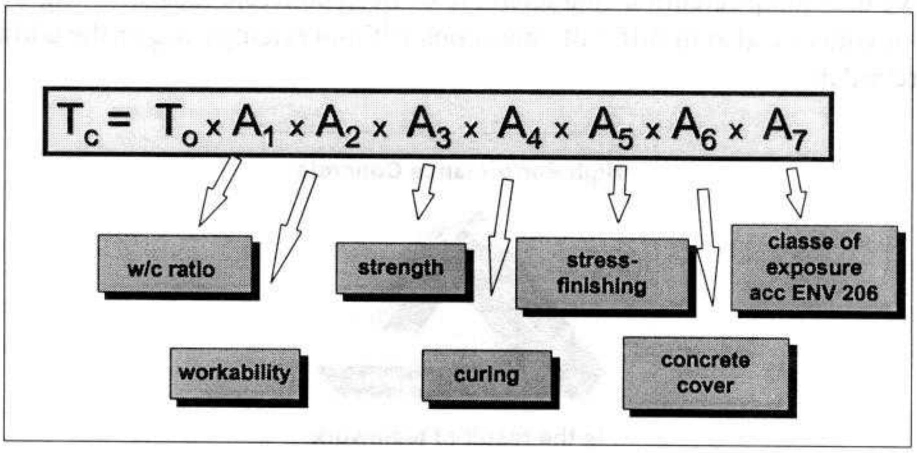
There are more definitions and suggestions for HPC, and it becomes clear that there is still room for further research in this field.

What is interesting is that the most of the affected parameters are directly influenced by the concrete's impermeability and porosity, both being influenced by its w/c ratio.

While we in the construction industry talk about "strength", "impermeability", "durability" and "performance" of concrete it boils down for the owner of a building to the question of "life time" or "life span". That is what he is interested in above all.

The CTE concrete life time calculation model (Table 9), developed in Italy, takes this concern into account.

Table 9. Life time of a concrete structure



As can be seen, the durability, or life time of a structure is not only a question of w/c ratio and workability but the formula shows clearly the influence of this two factors. Tables 10 and 11 give some more details about the two factors.

Table 10. Influence of w/c ratio

w/c ratio	< 0.45	0.46 - 0.50	0.51 - 0.55	0.56 - 0.60	> 0.60
A_1	**1**	**0,95**	**0,90**	**0,80**	**0,70**

The coefficient $\mathbf{A_1}$ is a function of the w/c ratio.

Table 11. Influence of workability

slump	< 4 cm	5 - 8 cm	9 - 12 cm	> 12 cm	rheoplastic
A_2	**0,80**	**0,90**	**0,95**	**1**	**1**

The coefficient $\mathbf{A_2}$ is a function of the consistency of the concrete during placement.

SUMMARY

High strength concrete is not necessarily durable concrete. In order to qualify for durable concrete or high performance concrete(HPC) certain minimum porosity and impermeability characteristics must be complied to. Today it is feasible to produce HPC.

The use of HPC is increasing rapidly.

High performance concrete (HPC) is the result of state-of-the-art concrete design, the selection of appropriate ingredients, controlled manufacture and placement. HPC is nothing magic, it is a "real" world affair but it does not happen by itself.

CE superplasticizers, thanks to their unmatched water reduction capability do help achieve the requirements of HPC by increasing strength and reducing porosity and permeability of concrete remarkably. In addition, and also that is unique for CE-based superplasticizers they improve the slump retention characteristic of fresh concrete thus allowing trouble free placement of concrete also in difficult conditions without retempering or the addition of undesired retarders.

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