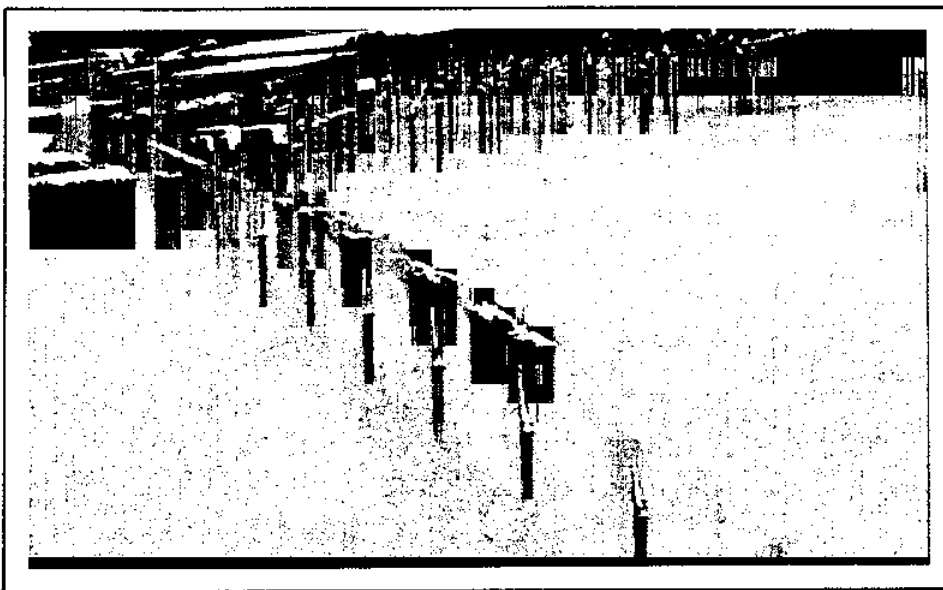


# Mario Collepardi Symposium

on

## Advances in Concrete Science and Technology



Cement and Concrete Science —  
The Twentieth Century Experience

by M. Moranville-Regourd

**Synopsis:** The twentieth century will leave behind many achievements in concrete technology. Only the materials science aspects of concrete are reviewed in this paper which describes the state-of-the-art with regard to superplasticizers, cement hydration, structures of hydrates at the nanometer level, and the colloidal chemistry of setting and hardening. Models of the microstructure of concrete have benefited from new techniques such as image analysis. Multiscale digital-image-based models are able to simulate transport properties. Concrete durability is still a problem in the areas of reinforcing steel corrosion and alkali-aggregate reaction. New types of deterioration processes such as the delayed ettringite formation are discussed. Some durability models are presented.

New materials have been developed through microstructural engineering. They are organo-cement composites, high-performance concretes, and ultra-high performance products based on reactive powder concrete technology.

**Keywords:** Concrete, cement hydration, superplasticizers, microstructure, models, durability, novel cements, high-performance concrete.

**P.K. Mehta**  
Editor

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## INTRODUCTION

Concrete is a material of great antiquity. Vitruvius (1) described it as "a species of sand mixed with lime and rubble,...it hardens as well under water as in ordinary buildings". The most famous concrete structure is the Pantheon in Roma. Hydraulic binders were used earlier by the Egyptians as mortars composed of sand and a burnt impure gypsum for the construction of the Great Pyramid. Hydraulic limes, mixtures of lime and pozzolana, appeared first in Greece, then in Italy and Europe. The "Pont du Gard", bridge and aqueduct, is a well known French example of durable Roman structures. After Middle Ages, surprisingly dormant-like periods, Smeaton (2), Vicat (3) and Apsdin (4) optimised and manufactured new hydraulic binders. One of them was named Portland cement. Research on characterisation and hydration of cements started at the end of the last century. Le Chatelier (5), Michaelis (6), Féret (7), Friedel (8) and Candlot (9) were pionners in the mechanism of initial cement hydration, development of mechanical strength and chemical durability. The 20th century and more particularly its two last decades brought important achievements. New products including water-reducing agents and fine particles were used in high performance concretes with high mechanical strength and enhanced durability. These new concretes called for new structural designs for bridges, tunnels and towers (10).

Our friend Professor Mario Collepardi was particularly involved in the field of mineral and organic admixtures. We are very pleased to honour him in Roma, having the sincere hope that he will be satisfied with new plasticizers (11). This presentation of concrete science is limited to concrete as a material recently improved thanks to new concepts, new techniques and new approaches to durability but material still partly unknown. The new concrete technology will be presented at this symposium by Professor Kumar Mehta.

## EXPERIENCE FROM THE TWENTIETH CENTURY

Advances in the knowledge of the composition and crystal structures of Portland cement minerals,  $C_3S$ ,  $C_2S$ ,  $C_3A$ ,  $C_2(A,F)$ , resulted from chemical (12)

and XRD analyses (13, 14). The refinement of structures of pure silicates, aluminates and their solid solutions were published in the Proceedings of the successive Symposia on the Chemistry of cement (Moscow 1974, Paris 1980, Rio de Janeiro 1986, New Delhi 1992, Göteborg 1997). Regarding the cement hydration, the understanding of the system  $CaO-Al_2O_3-H_2O$  was clarified but the  $CaO-SiO_2-H_2O$  system has long been discussed.

In his introduction to the Washington Symposium in 1960, Lea (15) said: "There is still much to learn of the kinetics of the initial reactions, of the part played by surface forces and of the mechanism by which the initial framework of setting cement is developed". At the same symposium, Powers (16) offered new approaches to the cement paste behavior showing that the physical study was "a bridge between cement chemistry and concrete technology". He considered first the flocculated structure of the cement paste in which solvated surfaces and electrostatic charges were important factors of the rheological properties, then the cement paste as a mostly colloidal and porous material. He brought in sight the distribution of water molecules depending on the relative humidity (free water at 100% RH, adsorbed water at 40% RH, condensed water in capillary pores at low RH) and the gel-space ratio versus strength. The permeability of saturated paste, drying shrinkage, maturity factor, freezing of evaporable water were also examined. The first model of the paste microstructure gave the distribution of cement hydrates and capillary pores at  $W/C=0.5$  and 0.3.

The flocculated paste which shows aggregations of particles with water inside flocs, themselves solid structures with a finite yield value in the static state, can be broken down by mixing or by surface active agents. In the seventies, superplasticizers appeared on the market and contributed, after Collepardi (13), to "the revolutionary developments in concrete technology".

## Superplasticizers

The first superplasticizers were by-products like lignosulfonates from the paper industry. Sometimes their variable composition induced undesirable effects, set retardation or air entrainment (17). So synthetic molecules were elaborated as polycarboxylic ether and cross-linked polymer (18), acrylic graft polymer (19).

The properties of superplasticizers are closely related to the composition and structure of the polymer i.e. molecular mass, degree of sulfonation, length of structural chains (20). Theoretical considerations have given details of their action (21, 22, 23). Polymers adsorbed on the cement particles disperse these particles by electrostatic repulsion, increase in surface potential, decrease in the surface tension of the mixing water, steric hindrance and modification of cement hydrates. The action of water reducing admixtures was studied through Zeta

potential and calorimetric measurements (22, 23). The initial reaction of the clinker interstitial phase gives a hydrated calcium complex including organic molecules, probably between cationic sheets like  $[\text{Ca}_2(\text{Al}, \text{Fe})\text{OH}_6]^+$ . Also, ettringite nucleates and grows as dense packing of short fibers (24) with no loss of workability. Admixtures are adsorbed on the surface of early hydrates, ettringite and C-S-H (25) and later on AFm with a loss of slump.

From a practical point of view, there is an optimum-molecular weight of admixture for the best fluidity, at a given W/C. A high molecular weight admixture is excellent at high W/C while a low molecular weight is preferable at low W/C (22). An optimum superplasticizer dosage corresponds to a saturation point (26). In fact, up to now, there is only one combination cement-plasticizer as the saturation point is different from one cement to another one, for a given plasticizer and from one superplasticizer to another one, for a given cement (17).

Superplasticizers used as water reducers increase both mechanical strength and durability. They can also reduce creep, shrinkage, thermal strains and bleeding if the amount of Portland cement is decreased or partly replaced by fly ash (27) or finely ground slag (28).

For a fully understanding of the action of superplasticizers more information is needed on the early hydration of cement. Plasticizers act as retarders to lengthen the induction period and as shown by proton NMR, adsorbed water molecules remain in their early state up to the end of the dormant period (29). After a XPS study, a retarder does not modify the first seconds of  $\text{C}_3\text{S}$  hydration (30). So plasticizers are mainly adsorbed on the first hydrates. In a Portland cement, the first sulfoaluminate is AFt or ettringite. Its crystal structure is well known (31). On the contrary, the hydration of  $\text{C}_3\text{S}$  is still in progress.

### Hydration of $\text{C}_3\text{S}$

**Kinetics:** The early hydration of tricalcium silicate, has long been discussed. The through solution theory close to the Le Chatelier's crystallisation theory (5) and the topochemical solid reactions in the Michaelis' theory (6) remained alternative suggestions during decades. Progressively, it was found that  $\text{C}_3\text{S}$  dissolved congruently after a superficial hydroxylation (32). However the kinetic of chemical reactions and the nature of C-S-H are still much debated. Besides the well known five stages deduced from the calorimetric curves of pastes (initial reaction, induction period, acceleratory period, deceleratory period, final slow reaction) (33), appeared two kinetic steps inferred from electrical conductimetry curves of stirred suspensions (34), the first one for lime concentrations in solution lower than 20mmol/l, the second one for lime concentrations higher than 20mmol/l.

Within ten seconds as shown by ESCA (30, 35) and by thermodynamic calculations (36, 37, 38), about 1%  $\text{C}_3\text{S}$  dissolves and a first hydrate, low in calcium ( $\text{C/S}\approx 1$ ) is formed on a layer of less than 1nm thick, more or less impermeable and non uniform. This hydrate is able to chemisorb  $\text{Ca}^{2+}$  ions and a second hydrate remains stable during the induction period. It has been called C-S-H (m), m for metastable (39). It acts as an effective barrier against  $\text{C}_3\text{S}$  dissolution. The end of the induction period corresponds to a through solution process. The acceleratory period is still debated. The growth of C-S-H (s), s for stable, appears as the rate limiting process instead of the portlandite nucleation in this third period. Then, in the deceleratory period, the diffusion of silicate ions through the C-S-H layer around anhydrous minerals is the rate limiting factor. Also the space available for hydrates is reduced. This is why the late C-S-H can appear as pseudomorphic with a finely grained homogeneous texture. In another approach (40) two kinetic steps following the lime concentration in the solution, correspond to two hydrates C-S-H (SI) and C-S-H (SII). The first hydrate covers  $\text{C}_3\text{S}$  grains when less than 1% of the silicate has been hydrated. The kinetic of the reaction is governed by the nucleation of C-S-H (SI). Then, up to 4%  $\text{C}_3\text{S}$ , the growth of C-S-H (SI) is predominant. When the rate of hydration reaches 13%, C-S-H (SII) appears. So, C-S-H (SI) grows as dimensional layer and C-S-H (SII) growth is three dimensional.

**Structure of C-S-H:** C-S-H was firstly called tobermorite gel then C-S-H gel. Discussions about its structure and composition arose between microscopists examining dried specimens and chemists analysing diluted suspensions. The nomenclature of C-S-H characterised by numerous investigators is still rather confusing.

The layered structure of C-S-H was first proposed in 1952 (41) from X-ray diffraction patterns. Foils and fibrous tobermorite-like crystals were observed under TEM in 1955 (42). It was more than thirty years later that Taylor (43) described a model with two C-S-H of a disordered layer structure containing ill-defined regions related to 1.4 nm tobermorite  $\text{C}_5\text{S}_6\text{H}_9$  for C-S-H(I) and to jennite  $\text{C}_9\text{S}_6\text{H}_{11}$  for C-S-H(II). More recent models were deduced from solid NMR studies. A high resolution  $^{29}\text{Si}$  NMR research was first published in 1982 (44). Then on the basis of CP-MAS (Cross Polarisation Magic Angle Spinning) able to distinguish C-S-H from anhydrous  $\text{C}_3\text{S}$  (45, 46), it was found that during the dormant period,  $\text{Q}^0$  species corresponding to isolated tetrahedra, probably hydroxylated, coexisted with  $\text{Q}^1$  and  $\text{Q}^2$  species. In  $\text{Q}^n$ , n is the number of tetrahedra bound to other tetrahedra, i.e.  $\text{Q}^1$  is a dimer that is a pair of linked silicate tetrahedra with a bridging oxygen.  $\text{Q}^2$  are in the middle of silicate chains. So, the structure of C-S-H is built on dimers and short silicate chains while the structure of tobermorite contains infinite dreierketten silicate chains. Several structures have been proposed depending on the C/S ratio: C-S-H with  $0.1 < \text{C/S} < 0.7$  and  $0.7 < \text{C/S} < 1.5$  (47) or C-S-H ( $\alpha$ ) with  $0.66 < \text{C/S} < 0.9$  and C-S-H ( $\beta$ ) with  $0.9 < \text{C/S} < 1.5$  (48). With increasing C/S, the polymerisation of silicate

groups decreases. The bridging tetrahedra  $Q^2$  disappear and give  $2Q^1$  sites which reduce the chain length. C-S-H has also been considered as a single phase with a structure varying continuously in function of the composition (49), but derived from that of tobermorite. Molecular dynamics simulation complemented NMR in the understanding of the rupture mechanism in the silicate chains when C/S increases (50). The rupture proceeds through the dissociation of water molecules after the incorporation of labile calcium atoms. The non bridging oxygens created by the dissociation are hydroxylated. In C-S-H with C/S=1.5, Si( $Q^1$ )-OH have been characterised by solid proton NMR (48). For C/S higher than 1.5, C-S-H is intermixed with CH. This limit is lower than the mean C/S ratio determined by SEM-EDAX which is approximately 1.7.

In his review of the nanostructure of C-S-H, Taylor (51) discussed the possible solid solutions of C-S-H and suggested that only traces of foreign elements could enter in the C-S-H in Portland cement. After NMR (52), molecular dynamics simulation and  $^{57}\text{Fe}$  Mössbauer spectroscopy, Al can substitute for Si and Fe for Ca in the structure of tobermorite but at a little level in C-S-H of high C/S with short silicate chains. These results are particularly useful for the study of cements leached by demineralised water. It has been shown that C-S-H with a C/S=1.7 dissolves but a new C-S-H with a lower C/S precipitates. Close to tobermorite this C-S-H is able to keep in solid solution iron and aluminium and remains stable (53)

### Setting

Theories of setting were first developed by Russian scientists. In 1926, Baikov (54) distinguished three stages (1) solution step, (2) colloidal step, (3) crystallisation step. Rebinder (55) also considered three periods: (1) dispersion of cement particles, (2) formation of a coagulated thixotropic structure, (3) crystalline structure precipitated from a supersaturated solution. Sschukin (56) showed that forces involved in the setting process were first Van des Waals forces in coagulation contacts, then bonds between adjacent crystals. The irreversible bridging to the force pressing the particles to each other has been discussed (57) and opposed to attractive particle interaction existing in pastes and suspensions. These interactions are due to the electrolytic nature of the pore solution responsible for the flocculated structure already stated by Powers(16). Coagulation occurs as soon as the calcium concentration in solution is higher than 0.1 mmol/l. Another possible mechanism based on the DLVO theory involves the formation of an electric double layer at the surface of solids in contact with electrolyte solutions. The stability of the suspension results from the combination of long-range repulsive forces due to the overlapping of double layers and the short-range attractive Van der Waals forces (58). Repulsive forces are low when the Zeta potential is nul but coagulation occurs when  $-25\text{mV} \leq \zeta \leq +25\text{mV}$ , depending on the concentration in calcium in the solution. However the

interface is always out of thermodynamic equilibrium and the ionic strength in solution is rather high. Solvation forces can be repulsive or attractive forces depending on the distance. They are attractive at short distance. Work is still in progress.

### Microstructure of cement and concrete

It is important to optimise a material before its use in a given environment and to understand the relationships between microstructure and properties. Complementary techniques offer the characterisation of the structural elements as particles, crystals, films, voids and of their juxtaposition and mutual arrangement. The microstructure of Portland cement and blended cements containing blast furnace slag, fly ash, natural pozzolana, silica fume and limestone fillers is now familiar to materials scientists (59) and has been largely presented in the Symposia on the Chemistry of Cement and ACI/CANMET international conferences. The historical development of microstructural studies includes the first observations by optical microscopy in the early years, by TEM in the fifties and SEM-EDAX in the seventies (60, 61). Different C-S-H were described by Diamond (62) as Type I in fibrous particles, Type II in reticular network, Type III in small equant grains, Type IV in inner product.

The first microstructure models pioneered by Powers (16) considered, besides the solid skeleton, the distribution of water molecules in function of the relative humidity and their role in creep, shrinkage or swelling (63). Inter-gel particle pores, intercrystallite pores and intra crystallite pore composed the pore structure of C-S-H (64). In the Wittmann's Munich model (65), the colloidal C-S-H ( $200 \text{ m}^2/\text{g}$ ) is termed a xerogel. The properties of the xerogel result from the strength of particles and their interaction with water. At high RH, the disjoining pressure of the adsorbed water films separate particles causing expansion and creep.

In the eighties and nineties, clearer images of the microstructure have been made possible through combination of techniques and careful preparation of specimens: high voltage transmission electron microscopy (HVEM), scanning TEM (STEM) of ion-beam thinned sections, backscattered electron images (BEI), analytical electron microscopy (AEM), environmental scanning microscopy (ESEM) equipped with a wet cell avoiding the drying of sample. Reevaluations of the microtexture gave new nomenclatures for cement hydrates as inner product and undesigned product (51) or phenograins and groundmass (66). A great progress came from the evaluation of the pore structure by image analysing (67) complementing other techniques like the mercury porosity, small angle neutron scattering, small angle X-ray scattering, helium flow technique, water vapor sorption isotherms (68), proton nuclear magnetic resonance (69). The large fractal dimension of the hydrated cement paste proved that the surface

of the material was extremely irregular and explained the differences in the surface areas evaluated by various sorption experiments (70). Quantitative image analysis, multi-scale digital-image-based modelling (71), computer based simulation modelling (72), automatic quantification of microcrack network (73, 74) were important steps to investigate the relationship between microstructure and properties of concrete and more particularly the autogeneous shrinkage, self desiccation and thermal strains leading to cracking, and the development of strength.

Early models of the microstructure considered the cement paste exclusively. Concretes are more complex due to the interfaces between matrix and aggregates. This internal transition zone, called "auréole de transition" in 1972 (75) differs in composition and structure, from the matrix, in usual concretes. It is better crystallised, more porous and less resistant than the matrix because of an excess of water. Also CH crystals oriente on aggregates. Recent models of the concrete microstructure reflect upon the porosity and connectivity of the transition zone and its role in the percolation characteristics and transport properties. (76, 77).

### **Durability of Concrete**

In an extensive review entitled "Durability of Concrete-Fifty Years of Progress?" (78) Mehta, in 1991, stated that "*today more concrete structures seem to suffer from lack of durability than was the case 50 years ago*". Concrete can be attacked by chemical, biological, physical and mechanical agents. The main causes of concrete degradation are corrosion of reinforcing steel, frost action and physico-chemical actions in aggressive environments. The permeability of the material appears as the most important factor of the deterioration. The ACI Committee on Concrete-Year 2000 (79) had already underlined, 26 years ago, "*irrelevant specifications and codes, wasteful and repetitive research and inadequate technology at engineering schools*". At the Atlanta Conference on Concrete Durability (1987) in their honour, Katharine and Bryant Mather gave us reflections on concrete durability (80) "*Concrete is international, it is made locally, it has infinite variability, it can be made to be very uniform. An unsolved problem is assessment of the nature and severity of the exposure, so that requirements can be graduated according to severity*". In that way were analysed the durability cases in Denmark and Australia by Idorn (81,82) or in Norway by Gjørsv (83) or in Canada by Pigeon and Pleau (84). In spite of thousands upon thousands papers or reviews, concrete durability problems still exist. Although basic research has been done on chemical attack (seawater, external sulfate, alkali-aggregate reaction) or electrochemical attack (steel corrosion by chloride ions or carbonation), concrete durability problems are periodically reported. Recent examples concern the sulfate attack and the alkali-silica reaction.

**Sulfate attack** New examples of sulfate attack appeared within the last decade in different countries and more particularly in steam cured concrete ties which exhibited large cracks after some years in service (85). The cause of expansion has long been discussed. "Delayed ettringite" and alkali-silica gels coexisted at cement paste-aggregate interfaces and were suspected of expansion either separately or simultaneously. Also the U phase was detected by XRD in concretes with a highly alkaline solution (86). Its formation has been shown expansive (87). Following discussions about the cause of expansion, a thermomechanical computation (88) applied to model concretes pointed out that elevated temperature curing can result in microcracking. The concrete tie was damaged in its thicker part with no visible alteration. The damage modified the elastic characteristics and more particularly the elastic modulus (89) and created mechanical stresses (90). So the "delayed ettringite formation" was an example of implication of curing temperature for concrete durability. Work is still in progress and a new RILEM technical committee named ISA, Internal Sulfate Attack, is chaired by Jan Skalný.

Another case of unusual form of sulfate attack, related to the formation of gypsum and thaumasite, occurred in the Canadian Arctic within two years of service (91). The source of sulfate was the ground water surrounding the concrete columns and the source of carbonate is suspected to be a fine carbonate in aggregates. Although this type of degradation has been observed in Europe (92), North American specifications do not consider it.

**Alkali-aggregate reaction.** The 10th international conference on alkali-aggregate reaction in concrete, held in Melbourne in 1996, has not solved all the problems as mechanisms of expansion or composition of gels. In fact there are a lot of alkali-silica products. Some paradoxes (93) appeared in the silica reaction related to the composition of the pore solution (alkali content, lithium concentration, presence of dissolved sulfate ions). Accelerated tests were critically reviewed (94): "*a completely satisfactory accelerated test method for determining the potential expansivity of aggregates in concrete, due to alkali-silica reactivity, has still not been developed, despite 60 years of research*". Some existing tests, mortar bar test, concrete prism test, autoclave test, need to be refined. In the assesment of AAR-affected structures (95), "*environment, or more precisely, changes in climatic and exposure conditions, is probably the most critical factor influencing and modifying accepted concepts of behaviour of AAR affected concrete*"

The mechanism of alkali-silica reaction has been approached by thermodynamics and kinetics of the chemical reaction considering the diffusion law. The reaction is initiated by OH<sup>-</sup> ions in the pore fluid (96), so sodium chloride is able to enhance both alkali-aggregate reaction and steel corrosion. New models predicting the expansion due to alkali-silica reaction consider

concrete as a heterogeneous reactive porous material (97) and reactive aggregates as spherical inclusions randomly distributed (98). The capillary pressure of expansive gels dissipated in connected porous zones initiate cracks which propagate following the linear fracture mechanics. The use of thermodynamics of irreversible processes (88), associated with the continuum damage theory (89), is able to directly get zones deteriorated by ASR in function of relative humidity and temperature (99). The effect of an external applied stress has to be validated by some experiments or in situ observations.

**Models of concrete deterioration.** Mehta (100), after a review of the science of concrete durability, offered a holistic model taking into account scientific data on chemical reactions and the knowledge of environmental effects on each component of concrete, the pore solution included. The first stage corresponding to the environmental action (weathering and loading effects) is able to microcrack concrete with no visible damage. The second stage corresponds to the expansion of concrete due to increasing hydraulic pressure in pores after the penetration of aggressive agents (corrosion of steel, sulfate attack, alkali-aggregate reaction, freezing). A holistic approach to concrete technology for major bridges has taken into account deterioration processes and their interaction (101).

The mathematical modelling of concrete durability has to be an incremental multiscale approach as the effects induced by chemical reactions are at the global level, deformations and cracks, but also at the local level, reactive sites, and diffusion through connected pores (102). Fundamental microstructural models use material parameters like the connected porosity instead of preparation parameters as degree of hydration, age or W/C ratio. The computer models are able to simulate degradation processes involved in transport mechanisms (103). It would be better to use material performance than material prescriptions in concrete science and concrete technology (104).

## MATERIALS FOR THE 21th CENTURY

Materials scientists have realized over the past decades that new high performance materials could be elaborated through a microstructure engineering (105, 106). Compared to materials like steel or sintered alumina, concretes develop low flexure strength and toughness, during their hardening. The weakness of these mechanical performances has been mostly related to the capillary porosity and to the excess of water needed for the workability of the fresh paste. Reducing the W/C by use of plasticizers or extracting the excess of water by pressure or filling in capillary pores by polymer impregnation were processes able to densify the cement paste and the transition zone.

## High performance cements

Pressure and vibration gave a compressive strength of 644 MPa and a total porosity of 2% in volume in 1975 (107). New products appeared in 1981: DSP, Densified Systems containing homogeneously arranged ultrafine Particules (108) and MDF, Macro Defect Free Cement (109). These new strong cement materials have been called CBC, Chemically Bonded Ceramics (110).

**DSP** contain Portland, silica fume and superplasticizers. First silica fume plays a physical role of filler. All solid particles are well dispersed by the superplasticizer and there is no bleeding. During the cement hydration, silica fume spheres are sites of nucleation (111) for cement hydrates and then react as a pozzolanic material giving an homogeneous and like amorphous C-S-H.

**MDF.** The densification of the cement paste increases compressive strength. However the material still exhibits a low flexure strength. A new approach of the porosity was done by Kendall, Howard and Birchall (112) who considered two pore families: capillary pores of volume  $p$  and cracks of length  $2c$ . Applying the Griffith theory of the fracture mechanics, there was a possibility for increasing strengths: reduce crack length. In the Macro Defect Free cement, a water soluble polymer disperses and lubricates cement grains in the cement paste suspension. The polymer being able to form a rigid setting gel, a strong mixing is necessary. During setting and hardening, the polymer dihydrates while cement hydrates. In the hardened material the polymer is highly bound to cement grains and the final porosity is about 1% by volume. The main characteristic of the microstructure is a dense and amorphous matrix around clinker grains. CH crystals are in thin lamellae distributed in the cement paste contrary to the large and thick plates in a Portland cement. Flexure strengths as high as 150 MPa have been related to the absence of large capillary pores and cracks. The moisture sensitivity has been improved by incorporating an isocyanate compound to cross-link the PVA molecules through urethane bonding.

**Organo-cement composites:** MDF can be processed without polymer. In an organo-cement composite, there is an interaction between cement and polymer as poly-vinyl alcohol, PVA, forming an interphase region (113) In a MDF made with an aluminous cement, the interphase is a thin rim, 5  $\mu\text{m}$  thick. Its microstructure is composed of nanocrystals of  $\text{C}_2\text{AH}_3$  embedded in a mixture of  $\text{AH}_3$  and PVA. Interphase and PVA form a continuous network.

MDF and organo-cement composites can be moulded, extruded and rolled as plastics. They can be used in composite materials containing sand, metallic powder, fibres which increase their toughness and resistance to

abrasion. Their water sensitivity due to the swelling of the polymer can be improved by using a cross-linking agent like an organotitanate or a silane.

**Belite cements and belite-sulfoaluminate cements.** Belite cements, belite-sulfoaluminate cements, calcium sulfo-aluminate cements are used for special applications like waste stabilisation or fixation of heavy metals. Such ecological cements will be presented by Kumar Mehta.

### **High performance concrete.**

Both characteristics involved in the mechanical strengths of concrete are the microstructure of the cement paste, including cement hydrates and porosity, and the nature of the cement paste-aggregate interface. In a DSP concrete (20% silica fume, W/C=0.16, Rc=160 MPa), fracture surfaces are transgranular with no cracks around aggregate and no CH oriented crystals at the interface (114). Strengths as high as 270 MPa were obtained with fused silica alumina aggregates (108). The total porosity measured by a mercury porosimeter is half that of a normal concrete. High performance concretes are now largely used on sites.

### **Ultra-high performance concrete.**

**Reactive powder concretes.** RPC were elaborated for ultra-high strength and high ductility.(115). Basic principles of the composition of RPC included the enhancement of the homogeneity by elimination of coarse aggregates, densification of the mixture by optimization of the granular distribution and application of a pressure before and during setting, control of the microstructure by post-set heat-treating, enhancement of the ductility by incorporation of small-sized steel fibers. Reactive powder concretes contain portland cement, silica fume and sand (average grain size 250  $\mu\text{m}$ ), crushed quartz (average grain size 10  $\mu\text{m}$ ). Their basic formulation includes OPC=1, Silica Fume=0.25, Water/(Cement+Silica Fume)=0.12. When quartz is used, it is at 40% by mass of cement. Some PRC were treated at 90, 200, 250 and 400°C. Some moreover were pressed under 625 atm. Thermal treatments increased the amount of bound water and pozzolanic reaction. Silicates hydrates were in function of temperature C-S-H, C<sub>2</sub>SH, tobermorite and xonotlite. The total porosity as measured by mercury intrusion did not exceed 9%. The porosity threshold is the smallest for samples treated between 90 and 250°C. No ettringite was detected after the heat treatment. Compressive strengths were 230 MPa for RPC treated at 90°C and 680 MPa for samples treated at 90°C and pressed under 500at. RCP 800 is expected to substitute for steel and has shown an excellent performance under the impact of projectiles. The durability factor has been found equal to 100 for different mixes performing in freezing and thawing cycles. The chloride ion

permeability measured by the ASHTO test translates a quasi-impermeability of the material.

## CONCLUSION

A vast amount of literature on concrete science has been published during the twentieth century; however, this paper has a limited focus. The author has chosen here to review only the progress in materials science and its application to concrete technology.

Toward the end of the nineteenth century, concrete science first benefited from a physico-chemical approach to studies on cement composition and hydration. Fifty years later, experimental studies on the physical structure and engineering properties of concrete were introduced. In the second part of the twentieth century, the basic research using new theories, some from colloidal chemistry or fracture mechanics, prevailed over the empirical science. The composite material was better understood through a fine characterization by sophisticated techniques like electron optical methods, image analysis, nuclear magnetic resonance, surface analysis, and porosimetry. Concrete was also improved in its rheological behavior by the use of superplasticizers. Concrete durability was an important topic of research. Models relating the microstructure to the macrostructure and properties under realistic environmental conditions are now being pursued.

New materials have been developed as a result of microstructural engineering. They are high-performance concrete and reactive powder concrete. Long-term durability, specifications and prediction of service life remain problems to be solved by the future generation of researchers.

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