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HYDRATION OF CEMENT:
STILL A LOT TO BE UNDERSTOOD

Despite the millenary history of the cement, several open questions still arise on the physico-chemical mechanisms underlying its hydration process. This short review addresses some of the most interesting open issues, indicating the main developing strategies for the investigation of this process.

A little bit of history

"*There is […] a kind of powder which from natural causes produces astonishing results. It is found in the neighborhood of Baiae and in the country belonging to the towns round about Mount Vesuvius. This substance, when mixed with lime and rubble, not only lends strength to buildings of other kinds, but even when piers of it are constructed in the sea, they set hard under water.*" (Marcus Vitruvius Pollio, Liber II, De Architectura, ~25 BC).

In these words the Roman engineer Vitruvius firstly described the properties of a material with surprising properties: a mixture of lime and crushed volcanic ashes was able to set under water, the resistance being increased along the time, in a way completely different to any other material. This "magic" material was called *pozzolanic* from Pozzuoli, the place near Vesuvio where the ashes were taken from.

The reason of the success of the Roman concrete was the substitution of the usual crushed stones (as Greeks, British people and the Romans themselves at the beginning were used to do) with volcanic ashes. According to the modern knowledge, a siliceous and aluminous material in itself does not possess cementitious value, unless it is calcinated and converted in an amorphous form. This calcination process, artificially produced in the modern times, was naturally made by the volcano for the Romans.

Nowadays, concrete is the synthetic material with the largest production on Earth: more than 11 billion metric tons are consumed every year all over the world. It is also one of the most complex inorganic systems. After more than a century of systematic studies, basic questions are still unsolved regarding its internal structure over the nanometer to macroscopic scale range, on its effects on concrete behavior, on the chemical and the physico-chemical mechanisms involved in the hydration reaction, especially in the presence of organic polymers. Most of these questions pertain to the primary hydration product and binding phase of Portland cement paste, the calcium silicate hydrate (C–S–H) gel [1].

What *"cement"* is?

Cement is a complex mixture of inorganic phases, mainly constituted by calcium silicates and aluminates. It is produced by heating a mixture of limestone and clay above 1450 °C. A few percent of calcium sulfate are added to the obtained nodules of clinker and finely grounded to produce the final cement powder. The major phases in a typical Portland cement are *alite, belite, aluminate* and *ferrite*. Alite is essentially tricalcium silicate (Ca_3SiO_5, C_3S) [2]: it generally constitutes 50-70% of the total mass. In conventional cements it is the most important phase, because it determines the setting time and the short-term strength development. *Belite* is dicalcium silicate (Ca_3SiO_4, C_2S, usually the β polymorph). It constitutes 15-30% of the whole clinker; the rate of *belite* hydration is very slow, thus it substantially contributes to the long-term strength development. *Aluminate* ($Ca_3Al_2O_6$, C_3A) and *ferrite* ($Ca_4Al_2Fe_2O_{10}$, C_4AF) are respectively the 5-10% and 5-15% of typical Portland cements: they chemically react very rapidly with water, forming a number of metastable hydrated species, that eventually transform over the time and convert to a final stable phase showing a cubic structure (C_3AH_6). The rate of *aluminate* reaction is so high that can cause a detrimentally rapid setting, unless a set-controlling agent, as gypsum, is added.

The hydration reaction

When anhydrous cement is mixed with water, a number of exothermic chemical reactions take place both simultaneously and successively, commonly denoted with the term *hydration* (schematically shown in Fig. 1). In the very first period after the adsorption of water on the surface of the dry powder, the dissolution of part of the inorganic phases starts to occur. Very soon, however, new silicate and aluminate hydrated phases begin to precipitate from the solution on the existing grains, thus favoring the further dissolution of the anhydrous phases through an incongruent process.
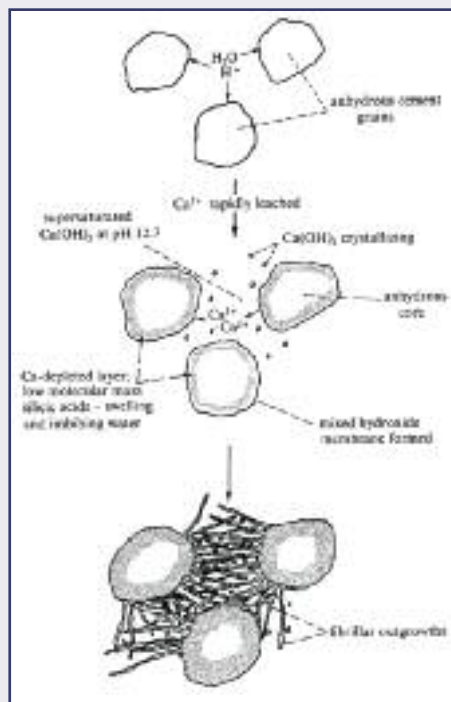
The hydrated phase responsible for the binding characteristics of the cement is an amorphous calcium silicate hydrate, called C-S-H, having the properties of a rigid gel. A secondary product of the hydration process is crystalline $Ca(OH)_2$, portlandite.

The reaction of the sili-

Fig. 1 - Schematic representation of the early stages of C_3S hydration

cate and aluminate phases with water is an exothermic process. In the literature five stages of product formation in C_3S and cement pastes are identified based on the heat evolution: a) the *initial reaction*, due to the early dissolution processes and to the very fast reaction of the aluminates with water; b) the *induction period* (or *dormant period*), lasting few hours, with a very low heat evolution; c) the *acceleratory period*, in which the nucleation and growth of the calcium silicate hydrate phase and of calcium hydroxide starts occurring rapidly and setting takes place; d) the *deceleratory period*; e) a period of slow, continued reaction, called *diffusional period*, because the rate of hydration is determined by the diffusion of reacting species from the solution through the hydrated phases, to reach the anhydrous grains.
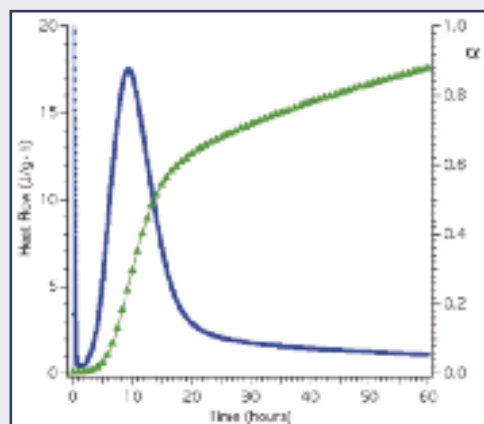
Experimental approaches

Fig. 2 - Heat flow (blue curve, left axis) and degree of reaction (green curve, right axis) as a function of time in the hydration of a C_3S/water paste (w/c=0.4)

The kinetics of cement hydration can be studied by following the variation of the degree of hydration, α, as a function of the hydration time *t*. A kinetic curve could in principle be obtained by summing the amounts of the individual phases that have reacted, for example by quantitative x-ray diffraction analysis (QXDA), but, because of the experimental difficulties and the limited precision, other indirect methods are typically used. The most used method to study the cement hydration kinetics is probably *isothermal calorimetry* (IC) [3-4]. The sample is placed in a bath with controlled temperature. The exothermic nature of the hydration process produces an increase in the sample temperature. The instrument records the temperature difference between the sample and the bath: this temperature gradient corresponds to the rate of heat evolution. The integration of this quantity gives the total evolved heat (Fig. 2). This technique allows both studying the hydration rate and calculating the activation energy. However, after a few days of hydration, the rate of heat evolution becomes too low to be accurately separated from the instrumental noise. Furthermore, as this technique requires a continuous use of the calorimeter, very long kinetics, such those produced by addition of some superplasticizers, can hardly be monitored for a time long enough to detect the acceleration period.

Another technique used to study the cement hydration reaction is quasi-elastic neutron scattering (QENS) [5-11]. A beam of neutrons impinging on a hydrating cement paste is scattered both elastically and inelastically. This scattering is almost totally due to the interaction of the neutrons with the hydrogens, because of its large incoherent

scattering cross section compared to the other elements present in the cement paste. The elastically scattered component has a Gaussian distribution in energy. The integrated intensity of this component is directly proportional to the number of non-mobile hydrogen nuclei, i.e. to the water chemically bound within the hydrated phases. The inelastic component exhibits a Lorentzian energy distribution, whose width is related to the state of diffusion (translational and rotational motions) of the hydrogen atoms. Thus, QENS enables to monitor simultaneously different water environments evolving during the hydration of a cement paste. First, the *bound water content* vs hydration time is obtained (Fig. 3A). If the stoichiometry of the reaction is known (as in the case of pure tricalcium silicate), this quantity is directly proportional to the hydration degree and thus to the kinetics of the process. The dynamics of the water confined in a solid matrix can be described according to the so-called "relaxing-cage model" (a detailed description of this topic is beyond the scope of this short review and the reader is invited to refer to references [12-14]). In this model the dynamics evolve during the hydration time according to a stretched exponential function: the values of the stretched exponent (β) and of the relaxation time (τ) show that the confining properties of the matrix increase in time (Fig. 3B-3C).

The big disadvantage of neutron scattering measurements is the very limited access to neutron sources that makes this technique inapplicable from an industrial point of view. Furthermore, a specific physico-chemical background is required for a correct interpretation of the experimental results. In the last years, our group proposed an alternative method, using Differential Scanning Calorimetry (DSC) to study the hydration process of cement. The progressive consumption of water due to the formation of the hydrated phases is monitored: the unreacted water is quantified, after different hydration times, through the integration of its melting peak and expressed as Free Water Index (FWI) (see Fig. 4) [15-17]. It is thus an indirect method, because it allows the reconstruction of the kinetic process through the disappearance of

one of the initial products. However it is a very simple and useful method as it provides a reliable way to determine the hydration curve of a cement paste particularly useful for applied research. One of the advantages in respect of IC is the intrinsic possibility to obtain the whole hydration kinetics with a very limited use of the instrument: our approach allows having a complete hydration profile up to 28 days using the calorimeter for 6 h only (30 measurements each lasting about 12 min). Moreover the intrinsic limitation of IC due to the low heat evolution after a few days is avoided and very long kinetics (for example those of pastes additivated with superplasticizing or retarding polymers) can be easily monitored.

Open issues in the cement chemistry research
Despite the millenary history, even after a century of systematic scientific research on the physical and chemical mechanisms underlying its hydration process and hundreds of engineering studies focused on understanding the rheology of the pastes and the mechanical properties of the cured cementitious samples, several questions are still open in the cement research.

C-S-H microstructure
One of the most important open issues concerns the formation and the composition of the cement structure, from the nanoscale up to the macroscopic scale. Most of the studies focus on the most important binding phase of Portland cement, the C-S-H gel. Several models have been suggested in order to account for its properties. The first models were based on the structural similarity with naturally occurring minerals, such as tobermorite and jennite [18]. All these models implicitly assumed that part of the silicate ions in the minerals were substituted by OH, in a random manner. Furthermore, because of the layered structure of tobermorite and jennite, the existence of interlayer spaces containing strongly absorbed water, was postulated. These models have been fairly successful in qualitatively
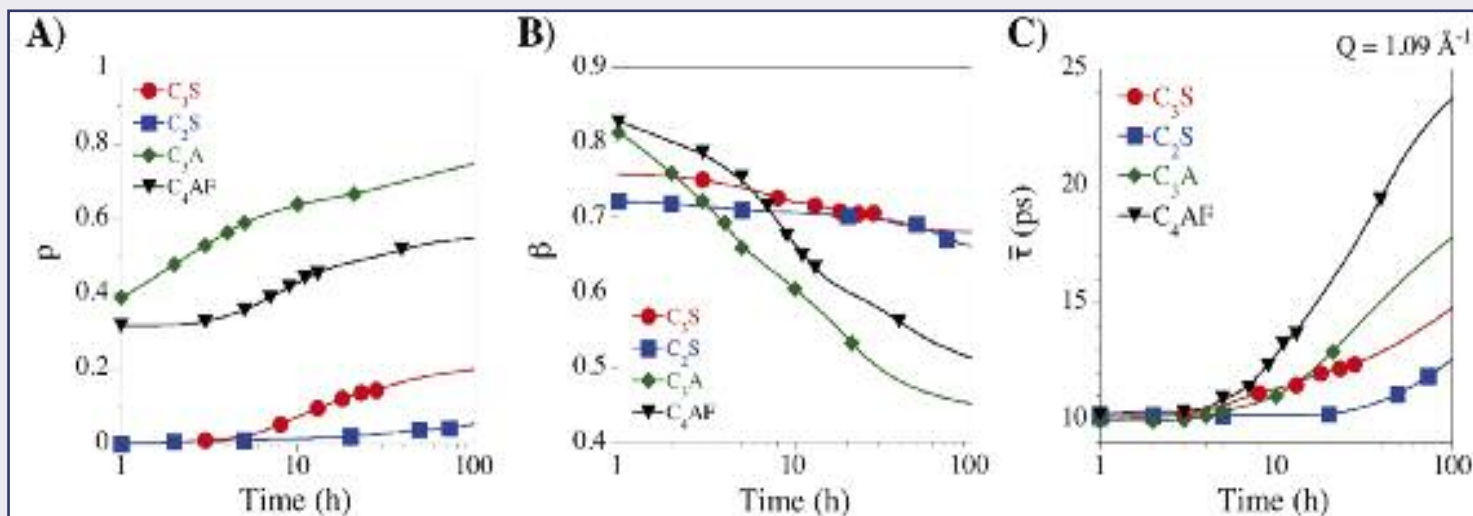

Fig. 3 - Time evolution of the QENS fitted parameters in the case of the four phases forming an ordinary cement powder (C3S, C2S, C3A, C4AF): (A) bound water (p), (B) stretch exponent, β and (C) average relaxation time, τ, at 25 °C. Reproduced with permission from Reference 10. © Institute of Physics (the "Institute") and IOP Publishing 2006
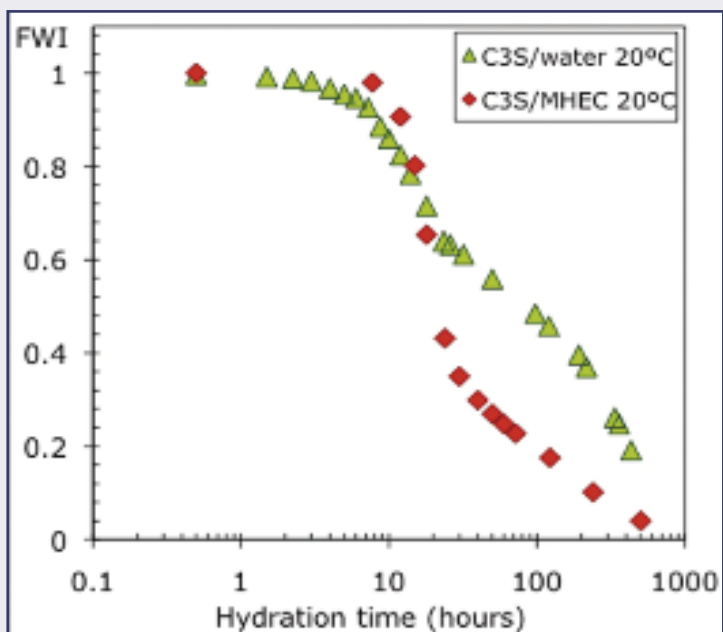
Fig. 4 - Free Water Index (FWI) vs time curves of C3S/water (△) and C3S/water/cellulose ether (◇) obtained by DSC. Water/cement=0.4, T=20 °C

packing densities, known as high density HD C-S-H, and low density LD C-S-H [23]. The first version of the model (recently referred at as *Colloidal Model-I, CM-I*) primarily focused on explaining how the properties of the material depend on the packing behavior of these basic globules [24]. In the description of *CM-I* model, the Jennings' effort was mainly directed to correlate the results obtained for the measurement of cement specific surface area by means of different techniques. As a matter of fact, because of the complexity of cement microstructure, conflicting experimental results are obtained when different methods are used to probe this feature [25]. In particular, the major challenge to the measurement of surface area arises from the very wide length-scale range of the microstructure internal features, from a few nanometers to tens of micrometers. Furthermore the cement surface area is an evolving property, depending both on the hydration time and on the curing conditions.

In the *CM-I* version of the Jennings' model, the influence of the globules' internal structure on the bulk properties was not explored in detail. Recently, *CM-I* has been modified and extended to take into account the smallest porosity of the C-S-H phase associated to the basic globules internal structure [26]. The *Colloidal Model-II, CM-II*, represents a significant improvement in the description of cement microstructure, since it reconciles many controversial data reported in the literature. In particular, this model gives an exhaustive interpretation of the sorption isotherms experiments. According to *CM-II*, the microstructure of a cement paste can be schematically described as in Fig. 5: the basic globule is a disk-like object, whose thickness is around 4 nm, having a layered internal structure. The water inside the globule is located both in the interlamellar spaces and in very small cavities (intraglobular pores, IGP), with dimensions around 1 nm. The packing of these globules produces a porous structure, where two other main populations of pores can be identified: the small gel pores (SGP), with dimensions of 1-3 nm; and the large gel pores (LGP), 3-12 nm in size. The inclusion of the sub-nanometric porosity in the model justifies most of the experimental evidences, representing a crucial step for the understanding and the control of the relationships between structure and properties (Fig. 5).

explaining the shrinkage behavior and gas sorption properties of cement paste. However they are insufficient to fully address the C-S-H properties, especially regarding the viscoelastic response of C–S–H gel to mechanical loading (creep) and the relative humidity changes (drying shrinkage).

Over the years the recognition of the colloidal and gel-like properties of C-S-H has progressively gained more and more importance. The first studies date back to the work of Powers and Brownyard, in the 1950s [19, 20]. They described the broad structure of the material basing their model on evidences from total and non-evaporable water contents and water vapour sorption isotherms. Their experimental results suggested that the product of the cement hydration was composed of solid units having a size of 14 nm, with nanometric gel pores. The colloidal description of C-S-H has been later included in other models [21] and nowadays it is definitely the most accepted, being the most appropriate to address the complex properties of calcium silicate hydrate.

A milestone in the development of the colloidal model for the C-S-H microstructure is the work published by Allen and coworkers in 1987, in which the microstructure of a hydrating cement paste was monitored by small angle neutron scattering. In that work the authors assessed the presence of a growing population of 5 nm gel globules, after the induction time. These globules successively were found to aggregate in structures with correlation lengths around 40 nm [22]. In recent years, based on the huge amount of data present in the literature, Hamlin M. Jennings in a series of papers formulated a clear and coherent model for the calcium silicate hydrate microstructure. The basic idea of the model is that the bulk microstructure is formed as a consequence of the packing of basic globules having peculiar shape and internal structure. Clusters of these particles group together in two
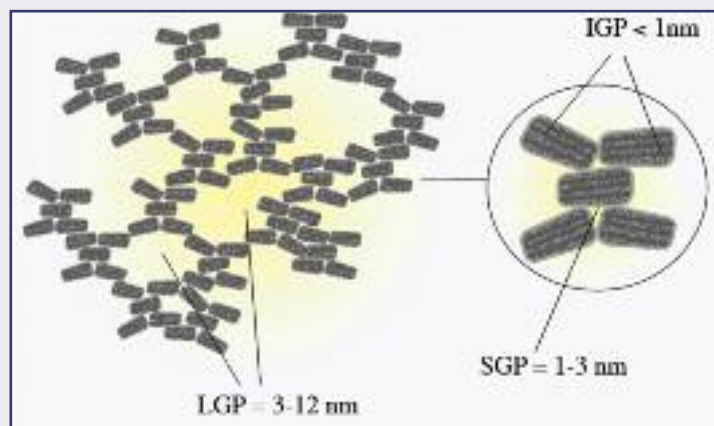

Fig. 5 - Shematic representation of the C-S-H microstructure according to the Jennings' Colloidal Model II (CM-II)
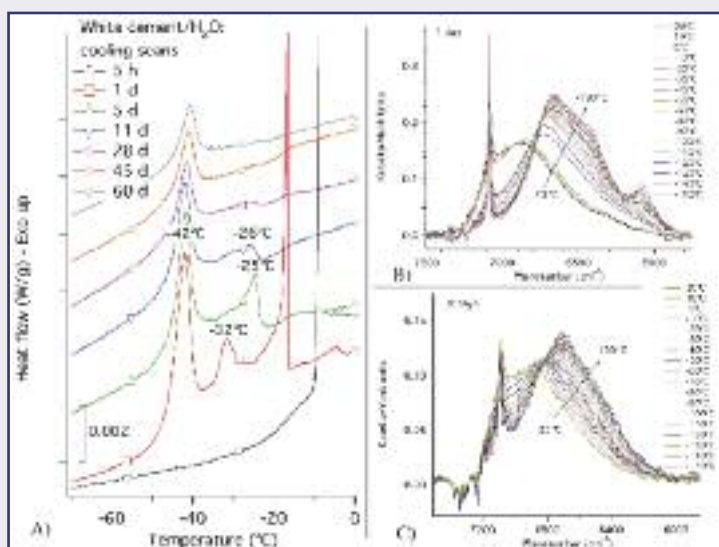
Fig. 6 - A) DSC cooling scans of cement paste cured for 5 h and for 1, 5, 11, 28, 45, and 60 days. The curves are offset for clarity. **B)** NIR spectra acquired from -150 to +20 °C on cement paste cured for 1 day. **C)** NIR spectra acquired on cement paste cured for 8 days

An alternative approach to the study of the cement paste microstructure evolution is to monitor the characteristics of the confined water throughout the hydration process. Very recently our group published a work in which the combined use of low temperature differential scanning calorimetry (LT-DSC) and low temperature near infrared spectroscopy (LT-NIR) enabled to investigate the properties of the water confined in a hydrating white cement paste [27]. The progressive confinement of the water inside the paste has been followed from a few hours after the mixing till two months of curing. LT-DSC thermograms show, upon cooling, several exothermic peaks in the temperature range -10 to -42 °C, whose position and area depend on the hydration process, as a consequence of the cement microstructure evolution (Fig. 6A). The peaks have been interpreted in terms of Jennings CM-II for the hydrated calcium silicate (C-S-H) microstructure. In particular the peak around -40 °C is attributed to the water confined in the Small Gel Pores (SGP), while the peaks in the region between -15 and -30 °C are due to the water in the Large Gel Pores (LGP). After a few days all the unreacted water is confined in the smallest porosity of the structure, as only the peak at -40 ºC is detected. The LT-NIR spectra allowed the investigation of the physical state of this confined water during the evolution of the paste. NIR is an excellent tool to study solid systems containing confined water, because it is very sensitive to small changes in the hydrogen bonds formed by water. The deconvolution in terms of Gaussian components of the 7000 cm^{-1} FT-IR band provided a detailed characterization of different O-H oscillators populations and their temperature evolution. In the younger samples, where the water is still able to crystallize, the Gaussian "fingerprint" of the hexagonal ice, centered at 6080 cm^{-1}, has been evidenced upon cooling and compared to data from the literature (Fig. 6B). As the hydration reaction proceeds, this feature disappears and the spectral deconvolution of the water bands discriminated the fraction of "sur-

face- interacting" water. In particular, we have shown that during the first hours of hydration the presence of the solid matrix does not affect the freezing behavior of the water phase, which crystallizes as hexagonal ice, whereas for longer hydration times (more than 8 days) the water confined inside the SGP porosity (1-3 nm) experiences important structural changes, remaining in an amorphous phase also at the lowest temperature investigated (i.e., -150 °C) (Fig. 6C).

This study provides a significant improvement in the comprehension of the microstructural properties of cement. Furthermore these results encourage a deeper investigation of the freezing-thawing effect on the mechanical properties of the pastes.

Mechanisms regulating the early hydration steps and the rate of the process

Another open issue in the field of cement chemistry is the description of the specific mechanisms that control the rate of cement hydration. This problem is particularly relevant for the interpretation of the influence of chemical agents, such as plasticizers, retarders, accelerators, on the hydration rate of cement paste [28]. Pure C_3S is often used as a model system for Portland cement, because the hydration kinetics and the properties of the hardened paste are quite similar. Several kinetic models are used in the literature to account for this process. There are numerous evidences providing that the early hydration period occurs by a nucleation and growth process, and kinetic data from C_3S hydration are frequently fitted to the Avrami-Erove'ev nucleation and growth equation:

$$\alpha = 1 + \alpha_I - \exp[-k(t-t_i)^M] \tag{1}$$

where α_i is the fraction of C_3S reacted (degree of reaction) at the induction time t_i, k is the rate constant and M is the exponent associated with the nucleation type (dimensionality of the product phase, type of growth, and nucleation rate). In the literature several papers report the application of this kinetic model in order to describe the effect of the water content [29], of the temperature [30, 15] and the influence of organic polymers [16, 17] on the hydration reaction of tricalcium silicate. As the nucleation-and-growth processes are temperature activated, the rate constants plotted against the inverse temperature follow an Arrhenius behavior:

$$\ln k = \ln A - (E_a/RT) \tag{2}$$

In this way the activation energy E_a of the process can be extracted and compared between different paste compositions.

Recently a new model has been proposed to better address the nucleation and growth kinetics of C_3S [31]. In this work J.J. Thomas focuses on the fact that the nucleation of the hydrated phases in the C_3S hydration is essentially a boundary phenomenon. As the Avrami-Erove'ev equation was actually formulated to account for bulk processes, a new *Boundary Nucleation and Growth Model* (*BNGM*)
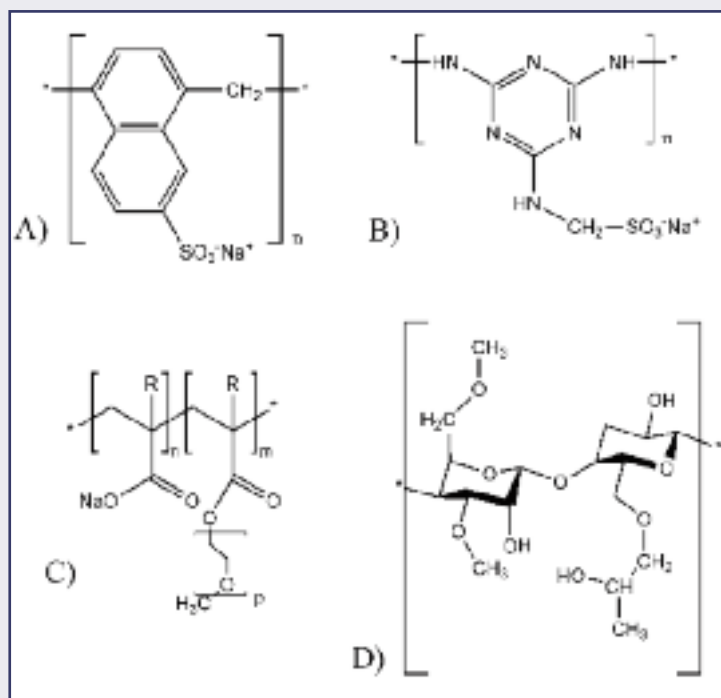
Fig. 7 - Some of the most used chemical additives.
A) Polynaphthalen sulphonic salts; B) Polymelamine sulphonic salts; C) Comb polymer with acrylic (R=H) or methacrylic (R=CH3) backbone and polyethoxylic side chains; D) Methyl HydroxyEthyl Cellulose

has been developed. This model was first elaborated for solid phases transformations occurring preferentially at grain boundary [32] and has been demonstrated to describe very well the C_3S hydration, introducing less parameters than needed in the Avrami model. According to the *BNGM,* the hydration process depends on two independent rate constants, associated with two distinct physical processes occurring during a boundary-nucleated transformation. Citing directly the Thomas' paper "k_B *describes the rate at which the nucleated boundary area transforms, while* k_G *describes the rate at which the non-nucleated "grains" between the boundaries transform*". The introduction of these two kinetic constants enables to include in the fitting also the induction period, demonstrating that this is not a separate chemical process, but it is simply a period where the overall hydration rate is very low because few nuclei have formed.

The refinement of the mathematical methods used to analyze the hydration processes of additives-containing pastes represents another interesting development of this topic. As previously said, the kinetic curves obtained by means of DSC can be monitored for very long times. In this way, thanks to the calorimetric method developed by our group, it is possible to study systems that are impossible to be analyzed by IC. When *BNGM* model is applied to fit the long kinetics of pastes additivated with superplasticizers, any k_B-k_G combination is found to describe the initial period of the process. For these systems the boundary-nucleation model has to be modified in order to account for the presence of a real induction period. Interestingly enough, the addition of high amounts of a cellulosic polymer does not require the use of a modified *BNGM*, even if the C_3S kinet-

ics is sensibly retarded: in fact, the kinetics of this paste is well fitted by the simple version of the model [33].

Modification of the hydration kinetics: addition of organic polymers

The modification of the concrete properties by adding small amounts of additives was a common practice since Roman times. For example, Romans used to add horsehair in order to enhance the mechanical resistance of the concrete.

Nowadays several kinds of organic polymers are commonly introduced in cement manufacturing to improve cement mechanical properties (i.e. workability and durability). These products are classified according to specific purposes and uses (water content reduction, setting time acceleration or retardation, fluidity enhancement, air entrapment, corrosion inhibition, water-proofing, modification of the viscosity, etc.).

In cement paste casting, sufficient fluidity and workability is needed. Both these properties can be improved simply by increasing the amount of water in the paste. Nevertheless, this operation causes two undesired side effects: a lower mechanical resistance in the hardened concrete and a lower resistance to meteorological alterations. In order to obtain fluid pastes, enhancing the workability and controlling the cement porosity, without increasing the water/cement ratio, chemical additives are used. These compounds are usually referred to as *plasticizers* and *superplasticizers (SPs)*. The use of these water-reducing additives in concrete began in the 1960s and nowadays is essential in concrete technology and in the field of construction. They are organic polyelectrolytes, used to improve the workability of mortar and concrete systems for demanding industrial applications. The first plasticizer used in industrial scale belonged to the class of lignin-sulphonated derivatives (LS) [34-37]. Very soon other chemical substances with better performances replaced LS compounds. The first-generation SPs were polynaphtalen-sulphonic salts (NSF) and polymelamin-sulphonic salts (MFS) [38-40] (Fig. 7A and 7B). The addition of low quantities of NSF or MSF produces high fluidity to the pastes: anyway an important drawback of these products was the fluidity decrease in time (*slump loss*).

Because of this effect, the technical advantage connected to their utilization was gradually lost in time. In the last years, a second generation of SP has been developed. They are *comb polymers* (or copolymers) with acrylic or methacrylic backbones and polyetoxylic side chains (Fig. 7C). These systems are able to maintain constant in time the fluidity of the paste [41, 42].

The effect of SPs on the hydration of Portland cement paste has been extensively studied, almost completely from an applicative point of view [41-44]. In the last years F. Winnefeld and coworkers carried out a systematic work by on the effect of the molecular structure of comb-shaped SPs on the performance of cementitious systems [41, 45, 46]. The effect of molecular weight, side chains length and side chain density on workability and on the early hydration
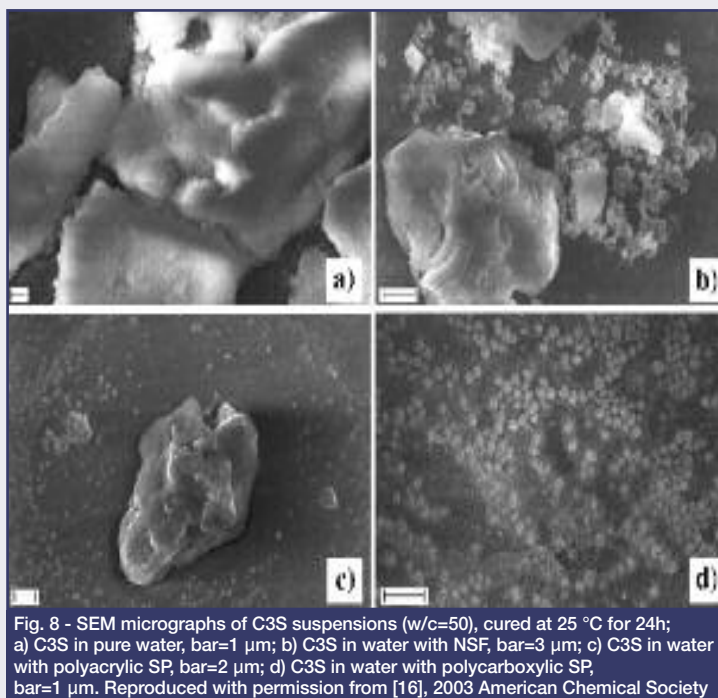
Fig. 8 - SEM micrographs of C3S suspensions (w/c=50), cured at 25 °C for 24h; a) C3S in pure water, bar=1 μm; b) C3S in water with NSF, bar=3 μm; c) C3S in water with polyacrylic SP, bar=2 μm; d) C3S in water with polycarboxylic SP, bar=1 μm. Reproduced with permission from [16], 2003 American Chemical Society

characteristics, as well as on the final microstructure and mechanical properties was investigated in detail. Some important guidelines have been finally drawn, very important from the industrial point of view, in order to tailor particular molecular architectures for specific applications. Nevertheless, one of the intrinsic difficulties in understanding the influence of the SP on cement hydration is the difficulty to have monodisperse polymers: very often their chemical formulae and their molecular weight are not well known, leading sometimes to confusing and contradictory results.

Despite their extensive utilization, the comprehension of the physico-chemical mechanism of SPs interaction with the cement phases is not yet complete. By means of calorimetry we studied the effect of SP (NSF, polyacrylic, polycarboxylic polymers) on the kinetic parameters of the hydration process of tricalcium silicate [16]. The kinetic analysis of these curves, by means of the Avrami-Erove'ev model, enabled us to obtain the activation energies for the nucleation-and-growth process of the hydrated phase, the M parameter (related to the morphological characteristics of the growing crystals), and the diffusional constants for pastes cured with and without SPs. The presence of additives produces a dramatic increment of activation energy value for the acceleration period, while the M parameter remains roughly constant. These results indicate modifications in the hydration mechanism, probably related to the morphology of the hydrated phase, as evidenced by SEM micrographs (Fig. 8) [47]. Since the activation energies are directly related to the nucleation process and, therefore, to the setting, their knowledge allows drawing a scale of additive efficacy, providing for the first time a quantitative approach to the field.

Cellulose ethers constitute another important class of organic poly-

mers used in the cement formulations. The use of cellulose-based polymers is increasing in the cement industry because their use often fixes many technological problems, mainly due to their interaction with water. In particular, they have been used as anti-washout or waterproofing admixtures, for the adhesive mortar production, and finally as viscosity-modifiers. This latter application is valuable in the *extrusion* technology. In the cement industry, the extrusion technique is mainly used to produce flat shapes with improved resistance to compression. Extrusion is a plastic-forming process that consists of forcing a highly viscous plastic mixture through a shaped die. The material should be fluid enough to be mixed and to pass through the die, and on the other hand, the extruded specimen should be stiff enough to be handled without changing in shape or cracking. These characteristics are industrially obtained by adding cellulosic polymers to the mixture.

In the last years we studied the effects of one of the best-performing cellulose additives (methyl hydroxy-ethyl cellulose, MHEC: see Fig. 7D) on the setting process of C_3S pastes. Water proton nuclear magnetic resonance relaxation experiments showed that cellulosic additives strongly interact with water and determine its availability to be consumed in the hydration process. The experimental results clearly show that cellulose additives act as a regulator of water release during the whole hydration process [48].

With the aim to understand the action mechanism of MHEC on the major pure phases constituting a typical Portland cement we obtained the hydration kinetics and compared the kinetic parameters (rate constants, activation energies, and diffusional constants) with those obtained for un-additivated samples. We found that MHEC addition in calcium silicate pastes produces an increase in the induction time without affecting the nucleation-and-growth period. A less dense C-S-H gel was deduced from the diffusional constants in the presence of MHEC. Furthermore, we studied the hydration products by using thermogravimetry-differential thermal analysis (TG-DTA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). We found that, in the case of the aluminous phases, the additive inhibits the growth of stable cubic hydrated phases (C_3AH_6), with the advantage of the metastable hexagonal phases being formed in the earliest minutes of hydration.

Despite its millenary story, the interest for this peculiar material from the scientific point of view is still growing: there's no other inorganic system exhibiting similar evolving properties, resembling in some aspects those of biological systems. Several topics that are still in progress in the field of the cement chemistry research are not covered in this contribute (for instance, the study of the forces responsible for the cohesion of cement pastes, or the identification of the relationship between macroscopic properties and nanostructure). Because of the complexity of the system, a multiplicity of approaches can be pursued. In this short review we selected only some of the most relevant topics currently ongoing in the scientific community, intentionally overlooking some other issues.

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Francesca Ridi got the Ph.D in Chemistry at the University of Florence in 2004. Her present Post Doctoral fellowship focuses on the study of the hydration reaction of cement, on the effect of organic additives on it and on cement microstructure, and on the physical and dynamical properties of water confined in solid matrices.

CRITICAL REVIEWS

RIASSUNTO

Idratazione del cemento: molto ancora da capire

Con una produzione di più di 11 miliardi di tonnellate di calcestruzzo prodotte ogni anno, il cemento è uno dei materiali sintetici più ampiamente utilizzati nel mondo. Nonostante il suo utilizzo sia noto fin dall'antichità molte domande sono tuttora aperte a riguardo della reazione di idratazione e costituiscono l'argomento di numerosi progetti di ricerca sia nel campo della scienza dei materiali, che nel campo della chimica-fisica dei sistemi colloidali.