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On the origin of cement setting, and how to control the properties of the fresh and hardened material.

Maurizio Bellotto[1]
[1]Giovanni Bozzetto S.p.A., Filago (Bg), Italy

Abstract. Cement paste forms an elastic gel immediately after mixing cement and water. The gel's strength rapidly increases during the dormant period. The cohesion of the gel originates from attractive forces among the hydrating surfaces and a network of nanoparticles of calcium-silicate-hydrate (C-S-H). These attractive forces do not vary throughout the dormant period, and cement paste stiffening can be interpreted as the result of an aging process occurring when cement paste is at rest. This aging process goes along with a refinement of the paste microstructure, with the large pores decreasing in volume. Shear interrupts the aging and brings back the system to its initial state, until the massive Portlandite precipitation occurring at the beginning of the acceleratory period initiates setting.

The microstructure of cement paste, which is at the core of both concrete strength and durability, is determined by the mechanisms of gel formation and by the coalescence of the cement and hydrates' particles into flocs which span the entire space. This comes to say that the porosity, strength and toughness of the hardened paste result from the intensity of inter-particle forces and from the kinetics of particle aggregation. It is widely accepted, even if not completely understood, that chemical admixtures modify these forces. It is thus possible to control the properties of cement paste, both in its fresh and hardened state, by using chemical admixtures which interact with the hydrating surfaces and modify their interaction potential. Most of such applications are already in use and have been developed with a trial and error approach, however the understanding of the forces at the origin of cement cohesion, and the knowledge of how to modify them may lead to the development of new, more sustainable binders.

1 Introduction

When Portland cement is mixed with water, anhydrous oxides begin to hydrate and the contact solution is enriched with Ca^{2+}, OH^-, SO_4^{2-} and silicate ions [1]. As the pH rises above 10, and the Ca^{2+} concentration exceeds 1 mM, the solution becomes supersaturated with respect to the precipitation of calcium-silicate-hydrate (C-S-H). After a rapid initial burst of dissolution and nucleation the rate of hydrate precipitation decreases abruptly and the cement paste enters the state defined as "dormant". The decrease in hydrate precipitation rate is attributed, among others, to the decreasing anhydrous phases dissolution rate brought about by the high Ca^{2+} and OH^- concentration in solution [2] and/or to the poisoning of the C-S-H nuclei surface by anions (e.g. aluminates) present in solution [3]. From the initial contact with water the paste develops elasticity [4-6], thus pointing to the presence of attractive inter-particle forces typical of attractive colloidal systems [7]. Here and in the following the word "colloidal" is used, maybe improperly, to refer to any situation in which surface forces are predominant, following the terminology in [8,9]. The attractive forces are induced by the precipitating C-S-H gel through its high surface charge density [10]. However the build-up of the hardened cement paste microstructure is not only due to hydrate precipitation [6].

The yield strain ε_{yield} of fresh cement paste is very small, of the order of 0,05% ÷ 0,1%: cement paste has a brittle behavior as a result of the short range of the interaction forces compared to the particle dimensions [5,11]. The storage modulus increases over time within the dormant period if the paste is not sheared [5,12]. If the paste is sheared or subjected to large amplitude oscillations well beyond the yield strain ε_{yield} the storage modulus decreases to almost the initial level, the exact value depending on the time elapsed and on the shear stress imposed. When the shear is stopped the storage modulus starts increasing again and the rate of increase is identical to what observed initially [5,12]. The continuous growth of G' in the dormant period has been attributed to the formation of C-S-H [5,13] and to the strengthening of the inter-particle necks [14].

If the microstructure of cement paste is described as fractal agglomerates of hydrating cement particles and newly formed hydration products [15,16], the evolution occurring during the dormant period may be interpreted as a refinement of the pore structure associated with a decrease of the fractal dimension, with large pores decreasing in volume [15]. The presence of admixtures does not change qualitatively the evolution, however by modifying the interaction between the hydroxylated surfaces it influences the viscous and elastic properties of cement paste. Properties like cohesion and resistance to bleeding, pumpability, stickiness and to a certain extent also the yield strain ε_{yield} can be controlled by the use of admixtures.

2 Microstructure of cement paste

2.1 At rest

The storage modulus of cement paste increases over time, during the dormant period, of more than two orders of magnitude, as it is shown in Fig. 1 for the case of a paste issued from a CEM I 52,5 R cement at two different water-to-cement (w/c) ratios. The precipitation of Portlandite, associated to the end of the dormant period, occurs for the paste investigated in the present work between 60 and 80 minutes, as measured by electrical conductivity and isothermal calorimetric experiments [15]. The increase of the elastic modulus during the dormant period is associated with an increase of stress-bearing contacts among the fractal clusters [17] related to the surface hydroxylation of the Ca-silicates and to the precipitation of C-S-H.

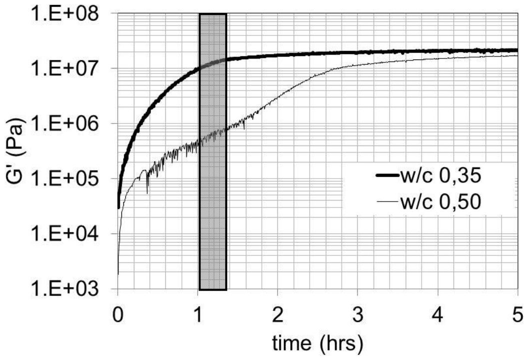

Fig. 1. Storage modulus of cement paste during the dormant period and in the early acceleratory period. The shaded area marks the approximate end of the dormant period.

The increase of the storage modulus is interrupted by shear, as shown in Fig. 2. The value of the storage modulus is brought back nearly to the initial value by the applied shear, and when the shear is stopped the storage modulus starts increasing again almost with the same kinetics as before. This behavior indicates that the cohesion of cement paste is originated by the same attractive forces during the dormant period, and that the microstructural modifications responsible for the increase of the storage modulus are reversible under shear. This last observation is expected since the precipitation of hydrates, and of C-S-H in particular, is negligible during the dormant period.

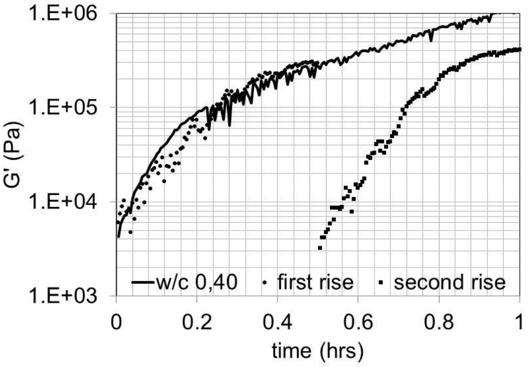

Fig. 2. Evolution of the storage modulus of cement paste over 1 hour at rest and with an interruption by shear after 30 minutes.

A difference is observed between the behavior of cement paste and the one of a paste of C_3S, as reported in Fig. 3. The shear is less capable of disrupting the structure of the paste in the case of C_3S, introducing an element of non-reversibility in the mechanical evolution. This non-reversibility is associated with the loss of fluidity observed under shear, the “slump loss”, and it is related to the lack of an induction period for C-S-H crystallization in the paste of C_3S [3]. When discussing the behavior of cement paste under shear this argument will be further discussed and quantified, suggesting that the non-reversibility or slump loss is associated with the growth of C-S-H crystals which resist breakage by shear.

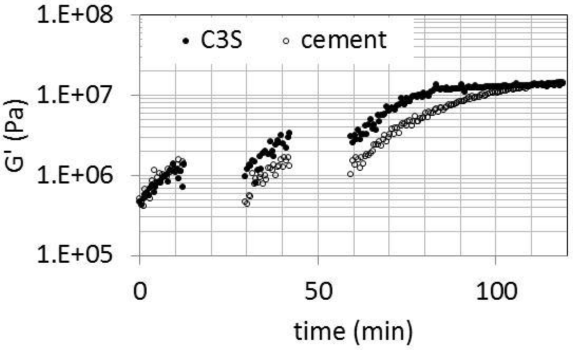

Fig. 3. Evolution of the storage modulus of cement paste and C_3S paste over 2 hours with two shear interruptions.

The fractal dimension of the agglomerates is quite high, around 2,8, as observed experimentally [18,19] and as can be derived from the observed dependency of the storage modulus versus the solids volume fraction of the paste, related to w/c [15]. The agglomerates are quasi-compact, although not homogeneous. The distribution of heterogeneities varies during the dormant period, a process which microscopically can be assimilated to the refinement of the pore structure, with the large porosity decreasing in volume.

When superplasticizers are introduced into the paste the gelation threshold is increased and a behavior similar to what observed for the neat paste is observed although at lower w/c, as indicated in Fig. 4. The elastic modulus scales with both the solids volume fraction of the paste and the inter-particle potential [7], and the observed behavior is an indication of the decrease of the inter-particle attractive forces brought about by the superplasticizers. No qualitative difference in the evolution of the storage modulus is observed between the neat paste and the paste in the presence of superplasticizers, indicating that the same forces are acting among the particles, even if of a different intensity.

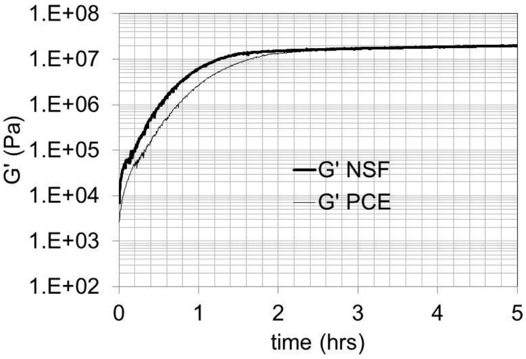

Fig. 4. Evolution of the storage modulus of cement paste at w/c 0,35 in the presence of superplasticizers. NSF stands for naphthalene sulfonate and PCE for poly-carboxylate ether.

2.2 Under shear

Cement paste is shear thinning at low to medium shear rates – up to ~ 10 s^{-1} – and becomes shear thickening at higher shear rates, especially at low w/c [6]. In Fig. 5 the flow curves for the paste of the same cement as discussed above are reported at various w/c.

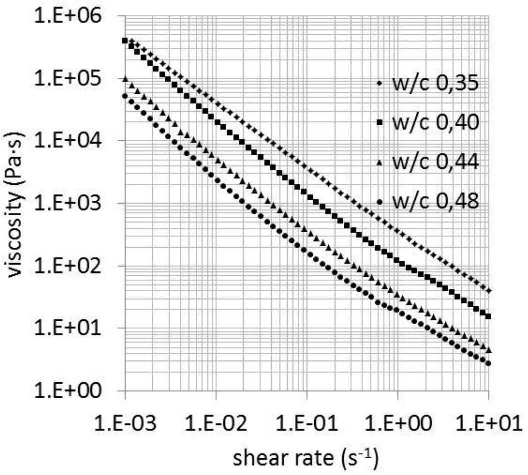

Fig. 5. Flow curves for cement paste at various w/c. The measurements are performed immediately after mixing.

In the framework of the description of cement paste microstructure as a network of fractal agglomerates as discussed above, the shear thinning behavior may be explained through the fragmentation of the agglomerates by the hydrodynamic field, making available the water initially trapped in the flocs. As time progresses and the C-S-H particles grow in size the agglomerates resist ever increasing stresses, and the flow curves shift upwards, as shown in Fig. 6 for the paste at w/c 0,4. This phenomenon is usually referred to as fluidity loss or slump loss. The critical strain to fracture the agglomerates can be deduced from the analysis of the flow curves [16], and it is shown in Fig. 7 for the paste at w/c 0,40. The critical strain can be related to the size of the C-S-H particles resulting in dimensions ranging from about 150 nm to about 600 nm as time progresses within the dormant period as shown in Fig. 7 for the same paste.

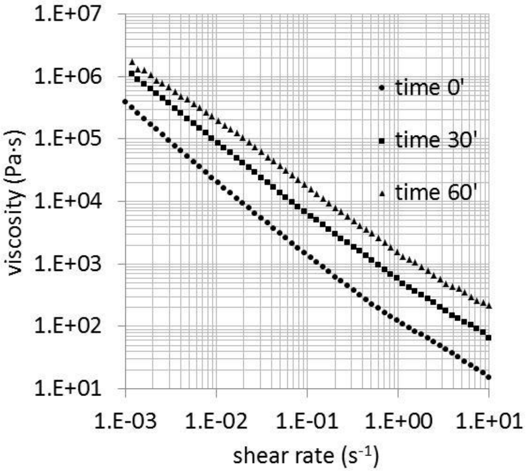

Fig. 6. Flow curves for the cement paste at w/c 0,4 at different times after mixing cement and water.

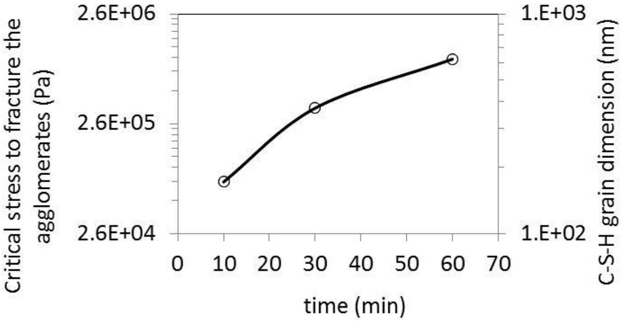

Fig. 7. Critical strain to fracture the agglomerates in cement paste at w/c 0,4, and the C-S-H particle size derived from it.

The flow curves of cement paste show the occurrence of shear banding at the lowest shear rates, suggesting the presence of a critical shear rate under which flow cannot be sustained homogeneously [20,21], as shown in Fig. 8 for the paste at w/c 0,4.

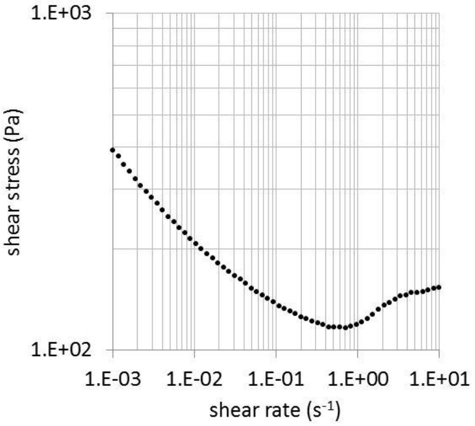

Fig. 8. Flow curve for the cement paste at w/c 0,4 expressed as shear stress vs. shear rate, showing the occurrence of shear banding for shear rates lower than ~0,5 s^{-1}.

The presence of superplasticizers has the effect of decreasing the inter-particle attractive forces, as discussed above, and thus of decreasing the critical stress to fracture the agglomerates, as shown in Fig. 9 in the case of pastes of C_3S without admixtures at different w/c, and with two different superplasticizers, a naphthalene sulfonate (NSF) and a poly-carboxylate ether (PCE). It appears that the PCE, a more efficient superplasticizer than NSF, decreases the critical stress with a lower amount of active matter, and it brings the inter-particle attractive forces almost to zero.

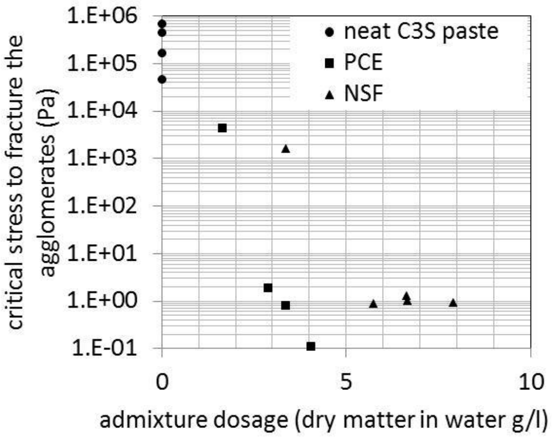

Fig. 9. Effect of the presence of superplasticizers on the critical stress to fracture the agglomerates.

3 Technological properties

3.1. Cohesion, segregation and pumpability

The main action of superplasticizers is to disperse the cement particles in the paste, thus achieving a high fluidity with low water-to-cement ratios. However it is common experience that secondary effects are often associated with their use, which occasionally limit the possibility to reach the desired performances. In the following the properties associated with paste cohesion will be addressed. In Fig. 10 are shown flow curves of mortars issued from self-compacting-concrete (SCC) realized with a PCE blended with varying amounts of lignosulfonate (LNS). Admixture composition and a subjective evaluation of the mortars is shown in Table 1.

Table 1. Fluidity and cohesiveness of a SCC mortar.

PCE (%)	LNS (%)	w/c	flow (mm)	cohesiveness	overall evaluation
0,24	–	0,475	430	very poor	very bad
0,24	0,09	0,500	445	poor	bad
0,24	0,18	0,500	425	sufficient	sufficient
0,24	0,27	0,500	390	good	good
0,24	0,36	0,530	405	excellent	excellent

On increasing the amount of LNS in the mortar – at constant PCE dosage – the flow decreases while the cohesiveness and the resistance to segregation improve. In the flow curves these modifications are evidenced by a reduced shear thickening behavior at high shear rates and a higher shear thinning behavior at low shear rates for the blends of PCE + LNS. In particular the high viscosity at shear rates ~ 10 s^{-1} observed for the PCE alone characterizes the stickiness of this mortar.

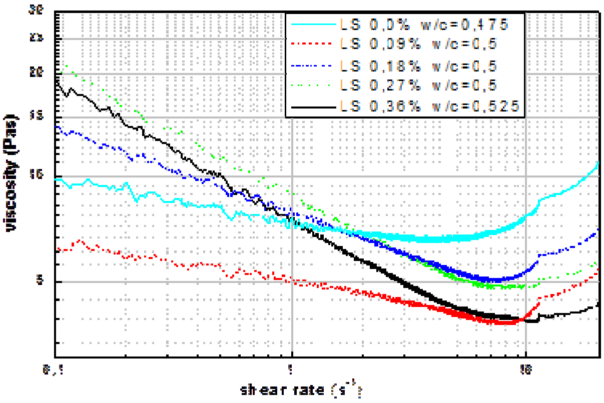

Fig. 10. Flow curves of the mortar issued from a SCC with different admixture blends.

The PCE alone and the blend 0,24% PCE plus 0,27% LNS have been measured also on cement paste, using the same cement employed for the SCC and for the mortar measurements. The results show that the critical shear rate, below which shear banding appears, is a steeper function of the paste concentration in the case of the PCE + LNS blend, as shown in Fig. 11.

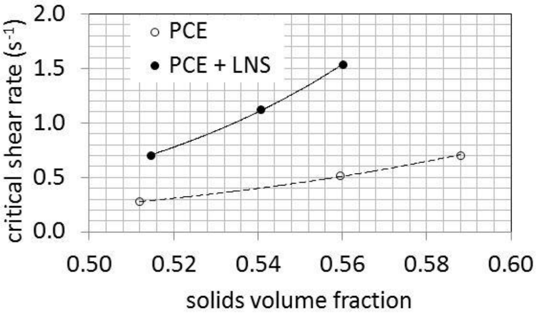

Fig. 11. Critical shear rate as a function of the solids volume fraction for the cement paste issued from the SCC.

Also the critical shear stress to rupture the cement agglomerates is significantly lower for the PCE alone than for the blend PCE + LNS, as shown in Fig. 12.

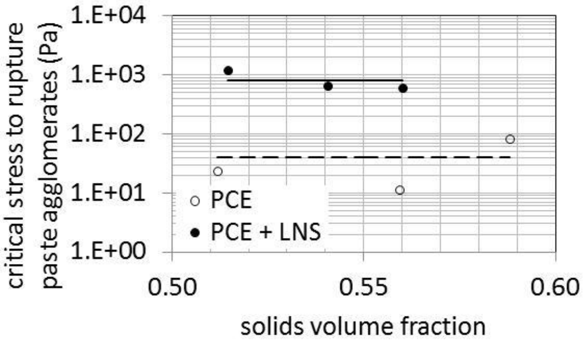

Fig. 12. Critical stress to rupture the cement paste agglomerates, with PCE only and with PCE + LNS.

It appears that the PCE is very efficient in decreasing the inter-particle attractive forces, but by bringing the interactions nearly to zero causes the loss of cohesion of the mix, at the concrete, mortar and paste level. With the PCE alone the concentration of the mortar and of the paste can be increased, and the w/c decreased, still having a high flow and a low yield stress but the overall feeling is of a sticky mass with a high viscosity at the higher shear rates. The low interaction forces among the cement particles cause the critical shear rate to remain low [20], causing an easier static segregation. The addition of LNS contributes to maintain the cohesion of the mix and to promote a low viscosity at the highest shear rates.

The same properties of cohesion and flow homogeneity are important to produce concrete to be pumped over long distances and high differences of level. In such a case concrete shall be stable with regards to static segregation and to dynamic segregation as well. Thus the cement paste must flow homogeneously without blocking at the highest shear rates, transporting the aggregates in the flow during acceleration or change of direction.

3.2 Yield strain and ductility

It has been mentioned above that cement paste has a very low yield strain, of the order of 0,05% to 0,1%. Moreover the yield strain is almost constant with paste concentration, as reported in Fig. 13 for the paste of the CEM I 52,5 R cement discussed above.

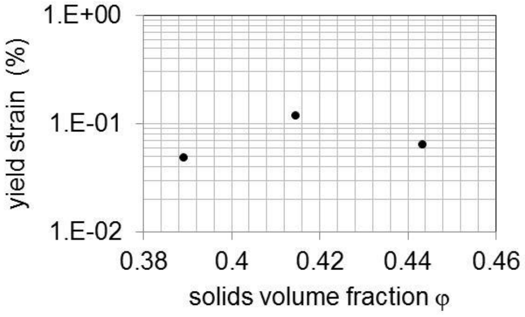

Fig. 13. Yield strain as a function of cement paste solids volume fraction.

This behavior is typical of attractive gels where the interaction forces are short ranged compared to the dimension of the particles. As a result cement paste is a brittle material. To compensate for the low ductility and low tensile strength reinforcement bars are currently used. However it has been anticipated, based on a modeling approach of the cohesive forces among the hydrating cement particles surfaces, that the presence in the mix of polymers would be able to modify the inter-particle forces, significantly increasing their range [22]. This theoretical prediction has been confirmed experimentally, showing that it is possible to increase by almost two orders of magnitude the yield strain, with only a minor modification of paste fluidity and rheological properties, as shown in Fig. 14. This would open the way to the development of more ductile concretes, more resistant to micro-cracking and necessitating less reinforcements to withstand tensile stresses.

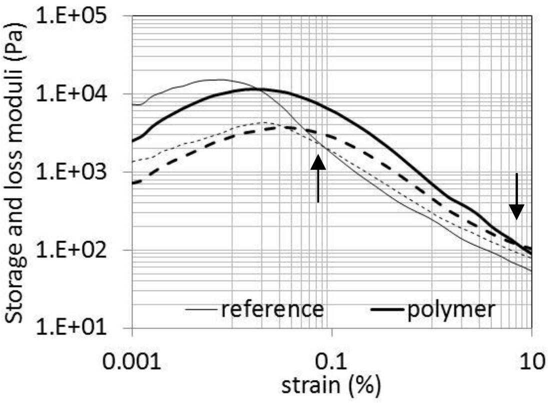

Fig. 14. Amplitude sweep for the cement paste neat and with a polymer. The continuous line is the storage modulus and the dashed line the loss modulus. The yield point is at the intersection of the two, marked with an arrow.

5 Conclusions

The technological properties of concrete originate from the forces acting among hydrating cement particles, both in the fresh state and after hardening. Cement paste forms a cohesive elastic gel from the very first moments after mixing cement and water. The strength of the gel increases during the dormant period because of the microstructural modifications associated with surface hydroxylation and hydrates precipitation, even if quantitatively the degree of hydration remains quite small. After setting, marked by the onset of Portlandite precipitation, a more pronounced microstructural evolution occurs, associated with the massive precipitation of newly formed hydrated phases.

The presence of chemical admixtures modifies the interaction forces acting among the hydrating cement particles, and thus enable the control of the mechanical properties and of their evolution over time.

Superplasticizers reduce the intensity of the attractive forces among cement grains, and consequently allow the increase of the solids volume fraction of cement paste at equal fluidity. The more efficient a superplasticizers is the lower the dosage required to decrease of a given extent the attractive forces. However when the attractive forces are reduced almost to zero, cement paste loses its cohesiveness, and it becomes inadequate for its purposes. Segregation of the aggregates occurs in concrete, and bleeding water separates from the mix. The cement paste loses its capability to enrobe the aggregates during the flow of concrete, and separation occurs during acceleration of the flow or during changes of direction. The inertial and collision forces become predominant at relatively high shear rates, above ~ 10 s^{-1}, and the mix becomes sticky, with a too high viscosity during flow, even if the yield stress and slump values are low and within the specifications.

Cement paste is a brittle material, because of the small range of the attractive forces compared to the particle dimensions. It is possible to increase the range of the attractive forces by introducing polymers competing for adsorption on the hydroxylated silicate surfaces. In such a way the yield strain can be increased by two orders of magnitude, imparting a more ductile character to concrete. Technologically this modification of the properties of hardened concrete is extremely significant since it opens the way to reducing micro-cracking and to a decrease of the use of reinforcing bars.

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