Materials Science and Novel Concrete Products

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Abstract

Progress over the last twenty years in the field of admixtures, new formulation methods and the use of fillers and ultra fines have led to spectacular developments in concrete technology. Compressive strength can be multiplied by ten times and more, liquid and gas permeability can be divided by 100 to 1000, rheological properties of fresh concrete can eliminate vibration. The latest developments show that combination of these properties is possible in true industrial production: ultra-high strength and ductility, high fluidity of fresh concrete and low permeability of hardened one, facing quality and durability, high performance and low standard deviation.

These developments will be illustrated through two examples:

- *Ultra-high performance concrete*: a technological breakthrough occurred at the start of the 1990s with the development of Reactive Powder Concretes (RPC) offering compression strengths in excess of 200 MPa and flexural strengths of over 40 MPa, with ductility. The result is that it is now possible to dispense with passive reinforcements in structural elements. The *Ductal*® range (developed by the BOUYGUES-LAFARGE-RHODIA co-operatively) was produced by concentrating on the multiscale optimisation of the material, which has resulted in a true ductile behaviour.
- *Self-placing concrete*: the new generation of superplasticizers, and a better understanding of rheological and chemical interactions of secondary cementitious materials enables the tailoring of new concrete mixes, changing the procedures of concreting and site organisation, as shown by the *Agilia*® range developed by LAFARGE.

Several recent applications will be illustrated and discussed.

Introduction

Over the last ten years, concrete has become extremely diversified thanks to the technical and scientific progress made using the most advanced tools the Science of Materials has to offer.

Although it is still the most simple building material to manufacture and implement, using basic raw materials, today’s concrete, through sophisticated formula methodology, has mechanical performances comparable to those of steel, show incredible resistance to physical and chemical deterioration and gives architects a quality surface and even larger architectonic possibilities. This article presents this material through two issues : the extraordinary capacity of concrete to meet more and more demanding requirements and the wonderful experimental field it constitutes for Science.

If concrete did not exist …

The yearly concrete production is, in both volume and weight, superior to all other material. Without concrete, we would be light years from achieving what is presently being achieved in construction work. It would be impossible to satisfy our ever growing needs for houses, schools, hospitals and roads, without concrete because there is simply not enough raw material available on our planet.

Concrete is inexhaustible as it is made from water, sand, gravel and, for cement, limestone and clay which are all ingredients available everywhere. Apart from a few islands in the West Indies or the Pacific, there are no countries incapable of having their own cement plants using local raw material. Concrete can even be made on the moon. Also, concrete can be recycled.

Therefore, competition with other materials is not an issue for concrete; it has to be used to its best advantage in association with the other materials. Its affinity with steel and the development of reinforced concrete is common knowledge. Its alliance with the highest performing steels in the 50's – giving prestressed concrete – has led to civil engineering's best achievements in the last 50 years. More recently (at the end of the 80's) appeared high performance concretes (HPC) with doubled or tripled mechanical resistance but which developed mainly because of their improved durability over time and their resistance against changes in water, humidity and agents of degradation. Without HPC, the construction of the Channel Tunnel, the Arch at *La Défense*, Paris, the *Store Belt* works in Denmark or the connections between the Japanese islands would have been if not impossible, at least, not as aesthetically pleasing.

Why is this considered to be a new situation?

It would be wrong to say that high-performance and long-lasting concrete did not exist in the past. There are some constructions dating back to the 19th Century which are still in good condition and will remain so (*e.g.* a building constructed in 1900 by HENNEBIQUE in Paris, rue Danton). The *Pantheon* in Rome, a work of art in building terms, has really stood the test of time; it is made of concrete and has all the ingredients necessary in chemical terms. The observation of the performance of these structures has helped and guided us in our research.

These performances, however, could not be exploited industrially because we did not know how to reproduce them, how to evaluate their resistance over time and, even if we had known, we would not have known how to explain the why or the how. As the client or his representative, the Contractor, could not demand these performances, a radically new situation has arisen today.

The Channel Tunnel is an example. When the construction experts of the Consortium in 1988 asked for proof that the concrete would last for 120 years with no alterations whatsoever, we were able to reply firstly by establishing a list of possible deterioration mechanisms then, for each mechanism, using high level measurable physics, prove its reliability beyond its required limits.

Another example: the United States and Canada are today confronted with a problem which is more and more difficult to solve: roads and bridges made from concrete which were not built according to the same high standards as in Europe, deteriorate very quickly and budgets for new work are nearly entirely taken up with reparation costs and the rebuilding of the existing network. The Transport Minister for Quebec made a brave decision in 1998. For the last two years, he has stipulated that in every bid it is specified that high performance concretes must be used for bridges and outdoor constructions as it is now known that these concretes are resistant and long-lasting. They cost a little more and add a little more strain to budgets but constitute the one and unique way out of an impasse.

This would have been inconceivable 15 years ago. Today an engineer has at his disposal tools, methodologies and software developed on a scientific basis, allowing him to define the optimal composition of material for a given application and to define the requirements of the Contractor in terms of utilisation. True material engineering which results in the convergence of two issues:

The knowledge of how to obtain a concrete which remains aesthetic and resistant over time within key parameters on the formula level as well as in implementation; these are operational methods, they are used on site and have proved their technical and economical efficiency albeit their use is still limited;

The development of a whole generation of mineral dusts and, in particular, organic products (especially polymers, which we call superplasticizers) which considerably increase the range of performances possible.

In two areas, the latest progress in concrete is spectacular:

- In implementation, with *self-levelling concrete*, which sets in place with no vibration (these days, a building site can be totally silent) and gives often very aesthetic facing: however, the success of these concretes is mainly due to a simple and rapid implementation and an important reduction in the time spent on sites;
- In *ultra-high mechanical performances* with which we will conclude.

It is important to note that aesthetic quality and duration are closely linked. Architects and historians explain that aesthetic assessment and taste are primarily the result of man's history and experience: it is because stone has resisted all these years that it appears attractive to us today. The same result does not always seem to apply to concrete as, in our heritage of construction, there are many beautiful structures but also many eyesores!

There are many ways today to significantly improve our environment each day at little cost. Cleaning, restoration, demolition and rebuilding costs lead to a considerable reduction in global costs.

Practically, however, there is a real problem in establishing long-lasting solutions as the construction market is based on a *lowest bidder* principle, which is inevitably detrimental to these solutions, even if this principle is accompanied by corrective measures. It has become urgent to standardise measurable indicators, correlated with maintenance costs and duration, in order to impose them in contracts. This is the way it began with cars and it worked. It has to follow for buildings and works of art. The stakes are much more important!

The scientific gaps that haven been overpassed

The scientific approach to a material as complex as concrete has been held back for many years for the simple reason that an astute comprehension of its performance cannot be achieved by the evaluation of a single scientific discipline. There are, in fact, a number of disciplines which have to be mobilised:

Firstly *Chemistry*: concrete has, for example, a element of magic in that, a few hours after having mixed the raw materials together, the mixture hardens by itself, the cement sets and, after the change, follows a procession of chemical reactions, the equations of which we know well;

Then comes *Physics*, with the practically miraculous element that the cement does not take instantly but only after 2 or 3 hours, which is particularly interesting on sites! This is Physical Chemistry with dissolving and dispersing processes on the surface of cement grains.

Thermal effects, which are generated by very strong heat from hydration, are very intense in the beginning and give complex physical and mechanical results;

The engineer who works out the structure, defines the dimensions of the girders, the section of the posts and scrap iron details makes mechanical calculations using *Mechanics of Solids* and *Material Strength.*

A number of gaps in our knowledge were filled when these different aspects could be examined under the combined efforts of one or more scientific disciplines which, in the History of Sciences, gave rise to the Science of Materials.

In his calculations, for example, the engineer has to consider two major particularities of concrete: *shrinkage* and *creep*, two particularities which are exceptional for a mineral material and which have always been a problem for the engineer who could not account for them correctly.

Shrinkage is a slow deformation, not very important, usually 1 in 1000. It is not perceptible to the eye but, as for thermal dilation, this distortion is often enough to cause cracks which can be very visible and can even jeopardise the life durability of the construction.

There are, in fact, always cracks on the concrete's surface but they are invisible to the naked eye. These cracks are due to the drying of the material as there is always some water wastage on the outside surface. Also, a beam or slab is always cracked because if the concrete does not crack, if the reinforcement does not form, then the structure is useless: <u>cracking is a normal part of the performance of reinforced concrete</u>. Cracking is even essential to the functioning of reinforced concrete.

However, the cracks must only be hairline so that capillary forces can fix the water fluid to block the ions which ensures a high level of pH to protect steel indefinitely from risks of corrosion. There is only a risk if the opening is more than 2 or 3/10 of a millimetre: if wider than this then water movement is possible and the ions ensuring a high level of pH can be dispersed. The whole theory of reinforced concrete is based on this argument and calculations are graded so that the size of the cracks remain within the critical size. This obviously works because the first construction works made on this basis have now been with us for more than a century.

However, if the shrinking is badly calculated, the cracks are larger than the critical size and consequences can be disastrous.

Creep is also a slow deformation, it is a deformation which follows the latter once the concrete is loaded. If shrinking has no significant effect on buildings and constructions made with reinforced concrete, this is not true for prestressed concrete where it can lead to a continual loss of prestressing, a loss which the engineer has to evaluate and make allowances for in his calculations. We know, today, that these two characteristics are both linked to the presence of water which is not chemically bound in the material, in the material pores and in the movement of this water in the pores. This is the area of Physics of Porous Medium.

Coupling : the missing link in Sciences

Engineers believe, as I have for many years, that it is sufficient to make tests, record the curves and enter them into the Mechanics equations. *EXCEL*, for example, does this very well: you enter the result figures, *EXCEL* produces a curve using these figures and gives you an equation. This is however of no value whatsoever as it does not show what to do for another scenario.

Here is a simple example which proves that entering physical processes through parameters belonging to mechanical laws is impossible. Below is the concrete part of the deck of the Normandy Bridge:

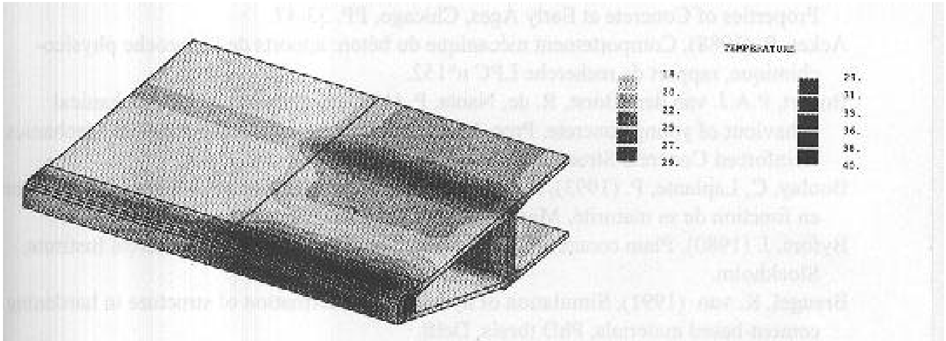


Fig. 7.Numerical simulation of the temperature in the segments

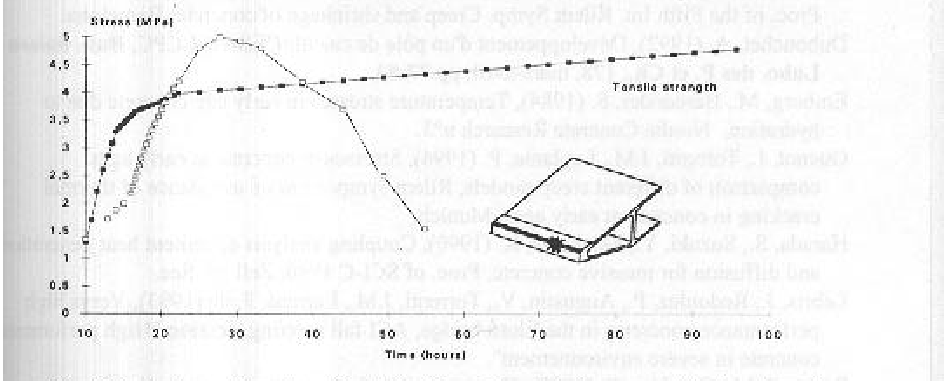


Fig. 1: Evolution of the stress compared to the strength

To ensure wind resistance, the bridge deck is designed like the wing of a plane and has solid parts at the two lateral edges through which the temperature, in the days following the pouring of the concrete, can go up to 60 or 70°C, because when cement sets there is a great deal of heat given off, ¾ of this heat within 10 hours. In construction, this phenomena is usually ignored because it is rare to have layers so thick and thinner layers cool down much more quickly.

Thermal laws prove (by dimensional analysis) that the cooling duration for a wall varies according to the square of its thickness, a wall 1-m thick, for example, will dry out in 10 days, a sail of 20-cm, 25 times less, will take a little less than 10 hours. In the former example, all the heat produced by the concrete setting accumulates in the centre of the part even before the outside has started to cool. In the latter example, the heat is dispersed towards the exterior and is given off more quickly than it is produced.

One can see by the example that the thinner zones heat less. Therefore the thinner zones will be put in traction with a risk of cracking. This calculation explicitly accounts for a thermochemical coupling, linked with an acceleration effect of the temperature on the kinetic chemistry and therefore on the flow of heat. This phenomena of auto-acceleration further amplifies the gradients of temperature and the scale effect.

This type of application has the ability to predict the temperatures to within one or two degrees in concrete construction works and the stress resulting, in certain cases, can be more important or critical than those due to the service load. This software is used to control that the original thermal tractions are still acceptable and, if not, to compare the efficiency and cost of the different technical solutions.

The engineer is therefore obliged to use a thermal calculation and cannot enter thermal radiation into his mechanical equations through a *"hidden parameter"*.

The effects of water and humidity are more complex, but my objective here is simply to explain two elementary mechanisms in order to understand and piece together the whole puzzle.

Why does water have such an important role in concrete?

To understand the basic mechanism of shrinking, we will use a very easy experiment, that of a capillary tube emerged into water. If the water enters the tube it is due to the fact that the surface energy between the liquid and the solid creates a damping angle (the only parameter involved being the chemical nature of the two bodies, solid and liquid), the meniscus curve. The more the meniscus curves, the more the molecules are unbalanced, the molecular forces working here cause a difference in pressure between the two fluids, liquid and gas, a difference which makes the water rise in the tube to a height which exactly compensates the unbalance.

So, if the tube is very narrow (if its diameter is inferior, typically, to 1 micrometer), then the pressure of the liquid is negative and the traction of the tube is on its inside. When one blows into a balloon, we increase the pressure which pushes against the inside wall of the membrane which, as we know, is taut. In the tube, it is simply the opposite: the water pulls on the surface which compresses the tube.

There is still, today, some reticence in accepting that water can exercise tractions of several megapascals. If water shows little resistance to shear (a deformation which can occur at constant volume), it strongly resists volume variations, whether in traction or compression. Concrete is a porous material, the pores of which (15 to 20 % of the total volume, *i.e.* 30 to 50 % in cement paste) can not be seen by the naked eye because of their size (from 2 nanometer to 1 micrometer, with a *fractal*-type shape and a peak value of 1.7 nanometer – the specific pores of C·S·H , the major product of clinker hydration).

If we measure the pressure in a blown-up balloon and its radius, we can calculate the tension of the membrane. In the same way, we know how to calculate the stress and the deformations resulting from capillary tensions in concrete. Pore geometry is more complicated, but today we have all the conceptual and numerical tools necessary to deal with it accurately.

Let's now see how the material is constituted, at least in the active phase – cement paste, how it develops from suspension to solid:

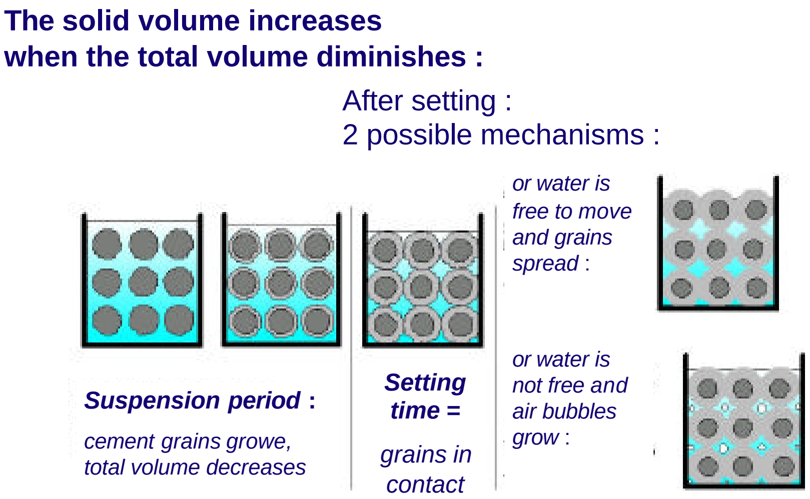


Fig. 2: Constitution of the material in the active phase-cement paste

The (apparent) shrinkage of material and the growing of hydrates has, for a long time, been considered as contradictory. In fact, by looking at the diagram – at least during the first phase – total volume can diminish even if each solid grain is growing. However, there comes a moment when the grains come into contact through a *percolation process* and once this threshold is crossed, there are only two possible solutions:

- either the water penetrates the interior to compensate for the decrease in volume, that is, if the water is free to move which is not always entirely the case! We do know nowadays that this process does exist on the surface but is limited to a thickness that depends directly on the concrete's density: centimetres in common concrete, millimetres in HPC;
- or gas bubbles appear or multiply in the material (in fact, it is basically an increase in the size of bubbles, which we call *entrapped air* because, when the concrete comes out of a mixer, the volume contains at least 1 % in little air bubbles).

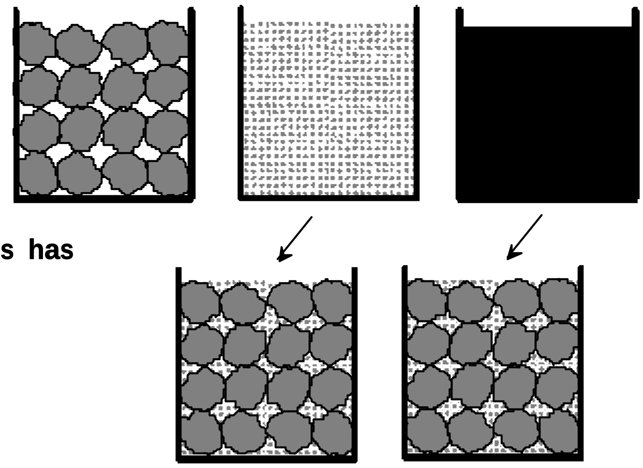
There is therefore a desaturation of the material. At one point, the bubbles multiply but do not remain spherical because of the size and geometry of the pores. The bubbles multiply and spread throughout the pores and finish by meeting up (another *percolation process*), generally after a few hours. The beginning of percolation shows up clearly with a hygrometric sensor embedded in the concrete, it is instantaneous which signifies that the connected gas phase very quickly reaches a balance with atmospheric pressure.

This is where the capillary tube mechanism comes in: the interface is a curve, this curve only relies on the geometry of the pores, is always well below a micrometer, water is stressed, therefore the mineral structure is under compression, which results in a deformation which constitutes *shrinkage*.

Another important step was made in the 80's when a theory for granular mixtures began. This theory was based on the following idea:

**All monosize aggregates have approximately the same void content and the same compacity,
which is approximately :**

$$C_0 = 0.60$$



But a mixture of several aggregate sizes has a slightly lower void content:

$$0.60 + 0.40 \times 0.60 = 0.84$$

$$0.84 + 0.16 \times 0.60 = 0.936$$

etc.

and :

$$1 - (1 - C_0)^n$$

where n is the number of granular sizes.

Fig. 3: Theory for granular mixtures

When the grains are all one size, there is always an important volume of empty space, approximately 40 %. This percentage is practically constant because homothety, in our space, preserves the volume relationship. The main property of granular mixtures is that, if we mix two types of grains of different sizes together, the density is significantly superior and has a tendancy, for a mixture of this type, towards a simple formula which can extend for mixtures of the n type and rapidly leads to 1, that being a total absence of empty space. Other factors should be taken into account, but this idea has led to the putting together of powerful mathematical models.

The first conceptual and technological *barrier* was crossed when a granular constituent, smaller than cement grains, was added to concrete and produced a generation of high-performance concretes. A second barrier was crossed when the continuous size range was completed down to the water molecule, which gave rise to the generation of the UHPFRCs, ultrahigh-performance fiber-reinforced concrete.

The first are not considered to be a truly technological leap as they are still quite fragile and do not eliminate the need for metal frameworks. However, they are used today when a life span has to be ensured (*i.e.* the examples in Canada and cross-Channel) or when the mechanical performance has to be very high (as an important reduction in shrinking as for the pylons of the Normandy Bridge.

The second, however, for example *Ductal*®, which thanks to a very high performance matrix (more than 200-MPa under compression) and fibres, is not fragile and allows the suppression of passive reinforcement, opening a whole new world in civil engineering and architecture in terms of lightness, durability, structure and aesthetics: the *Sherbrooke* walkway, in Canada (photo), cooling towers for nuclear power plants, etc.).

Fig. 4: Bridge made of self compacting conrete

With material such as *Ductal*®, for example, we have made significant progress in the comprehension of the material, without a doubt the most spectacular being the highly powerful methodology of analysis that resulted from Micromechanics, the *nano-indentation* method:

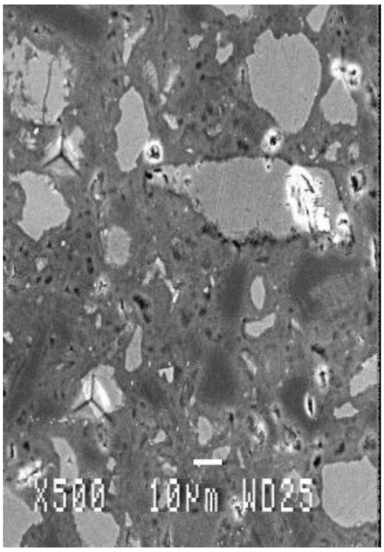


Fig. 5: Scanning electron microscopic representation of *Ductal*®

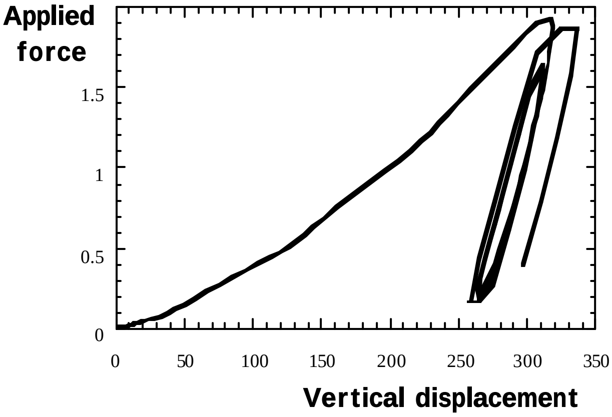


Fig. 6: Applied force vs. vertical displacement

This test consists of driving into a polished surface a small tetrahedral needle, the size of which is inferior to the various chemical type grains found in cement. We apply an increase in force and measure the vertical movement of the needle. After a few cycles of load and unload and bearings under load, we acquire three elements which characterise the mechanical performance of each element entering the microstructure of the material:

- the *elastic* part, with the slope at the first unloading,
- a *plastic* characteristic with the non linear element at the first loading,
- a *viscous* characteristic, with the speed of deformation at one of the levels.

Examination under microscope then permits the association of a recorded curve to each mineral species.

This methodology has shown that only C·S·H (hydrated product formed by a chemical reaction between water and the silicates of a clinker), flows significantly and that, for high-performance concrete and especially a material such as *Ductal*®, only the periphery of the grains are self-hydrating, hydration stops when the water of the capillaries runs out and the heart of the cement grains remain intact.

The anhydrous residues from the cement grains then act as elastic and not viscoelastic inclusions, with a high modulus of elasticity, superior to 100 MPa. Because of this, not only is the hydrate volume weaker (and the total creep is weaker) but also its spatial recovery around the grains, which occurs during external loading, and the recovery (*viscoelastic*) of stress (a characteristic of composite materials) leads to *stress concentration* and the stress fields lean towards the dry granular skeleton, which is the size of a dry granular structure, complete with an inert (non reactive) granular component which corresponds to the anhydrous residues in cement grains.

These results have led to a comprehension of the origins of creep for all concrete (which occurs significantly less with HPC and practically never with *Ductal*®) but also one last badly conceived aspect of shrinking (shrinkage continues after hydration: it is a *flow* of hydrates under the permanent stress of capillary tension). We now have a complete description of mechanical performance and this description has given rise to a *mix-design* methodology and tools that are today used in every area of construction.

Conclusion - Concrete, paradigm of a *Science of coupling*

The Science of Materials constitutes today a veritable scientific procedure, specifically for complex material, associating several sciences and combining methods and novel concepts.

Among these disciplines, there is one which is new, original and plays a specific role: Micromechanics, *i.e.* the Mechanics that we use on a microstructure scale, a scale where the various chemical elements can be identified, the exchanges between the phases, and a complete description of *physical mechanisms*. The microstructure is the place for discussion between representatives of the different scientific disciplines, where *coupling* can be observed and demonstrated. The concept of coupling gives structure and status to the Science of Materials.

If for a long time considered to be a dirty, unapproachable material, resisting all scientific approaches, concrete today stands out as being an archetype (I would even dare to say a *paradigm*) of the Science of Materials because it is the only material to mobilise all the disciplines in its constitution and because it gives the concept of Micromechanics a major role in this novel Science.