Chapter 5

Gluing and Composite Materials:
Concrete Admixtures

We have seen in the last three chapters that organic materials play a complementary role in civil engineering techniques, with respect to other classes of material, on the two aspects commonly experienced by users of *cohesion additives*, i.e. mainly as binders on the one hand and on the other as *plastic* or rather manufactured products, to which we have added industrial wood.

The first aspect is more complex. Adhesion involves several partners who are not always in perfect harmony. There is often even competition involved, as seen with respect to bitumen where adhesiveness in fact concerns the preferential wetting of the aggregate for bitumen in the presence of water. Notions of adhesion and adhesive bonding or gluing have been evoked several times, but for the study of the utilization of organic material based on a physico-chemical approach, it seems important to develop the subject in a specific manner.

When we speak of plastic, we normally imply qualities of flexibility, lightness and freedom of shape. However, flexibility goes hand in hand with its enemy, mechanical weakness. The recent development and appearance of organic matrix composites provide an original answer to the question. It is interesting to dedicate a few lines to the same, by pointing out that the significant amount of global scientific research taking place at the moment on this subject is almost exclusively on the mechanical aspect. The physico-chemical aspect does not appear very much.

Lastly, it is interesting to note that due to the existence of water-soluble organic polymers, hydraulic concrete technology was capable of making considerable and

unimaginable progress. Rheological admixtures have proved to be real cohesion additives acting as "third degree materials" and essential for present day concrete.

5.1. Gluing and its potential applications in civil engineering

Gluing, an assembly technique known since time immemorial and developed in all sectors of human activity, is presently not very much used in civil engineering. And yet the engineer is always on the look-out for the best combination of the existing techniques in order to obtain constructions which are cheaper and more comfortable. Gluing forms a part of these techniques and should find its legitimate place. Taking these conditions into account, we felt the need to dedicate one chapter to this type of assembly, where organic binders play a fundamental role, and being aware at the same time of the difficulties encountered and the limited nature of the concerned applications. We will therefore consider gluing as an innovative process, even though this expression should make you smile since we know that it is a very old technique.

The fact is that materials and techniques evolve, that the adhesives available today are different from those available 20 years ago (not mentioning those of our ancestors), application techniques have also evolved and finally there is also a great change in the way glued assemblies are used today. Problems which appeared blocked on the technical point of view need to be readdressed periodically. One of these is the use of gluing in civil engineering.

As of now, gluing is not considered to be a reliable method of assembly by technicians in the building and civil engineering fields: both engineers and architects do not have faith in this technique [MOU 99]. In order to progress in this debate, it will be interesting to start with a few thoughts on the subject from a physico-chemical point of view.

5.1.1. *Gluing: a future technique in civil engineering?*

Present gluing applications in civil engineering essentially concern structure repairs or reinforcement. The most well known technique is the repair of structures in concrete by gluing sheets as per the L'Hermite process which is presently evolving to steel being replaced by carbon fiber reinforced epoxy composites (see section 5.2.4).

In the area of new constructions, and particularly so in civil engineering, we are beginning to examine the possibilities offered by gluing as an alternative method to mechanical fixing of concrete on metal (mixed bridge connectors for example) or

metal on metal (tubular structure). The last case may also extend to changing the welding technique, which is recognized as a rough process for steel. But gluing can also be considered as a method of construction from prefabricated elements. Most importantly, the joint must be made to work in favorable conditions.

Let us consider the hurdles, which block at various degrees, the development of gluing as a technique for civil engineering and which can be summarized in the following questions: what kind of durability and safety can we expect? To this aspect we must also add a cultural block: we have no faith in gluing for construction purposes even though we fly in aircrafts where wings are glued, and we use cars where organic materials are found everywhere, even in the engine, and where gluing is greatly used.

Let us first examine the durability problem.

A durable glue joint is first and foremost a well designed glue joint. This assumes that the design rules and the limits imposed are well known and put into practice, use shearing stress instead of tensile stress and control the range of operating temperature as much as possible.

The first requirement is addressed mainly to designers and the second to adhesive manufacturers: an adhesive manufacturer must be able to respond concretely to well prepared technical specifications. Today, at least with respect to manufacturers, there no longer seems to be the problem of finding the adequate adhesive. There is therefore good reason to concentrate our efforts on precise definitions of requirements.

Next, a durable glue joint is a well made glue joint. Here we come across an important difficulty, common to all the techniques of utilization of organic binders, specifically the *qualification of applicators*. In the construction field we find as many specialists capable of working miracles as under-qualified personnel who prefer to use proven methods and are reluctant to try out alternative rarely-used techniques.

A well made glue joint in fact requires that great care be taken of:
− surface preparation;
− glue preparation (if it refers generally to a bicomponent);
− hardening (or curing) of the glue; this operation being often shortened arbitrarily for immediate cost-saving reasons ...

Even when the required conditions have been fulfilled, total success is not always obtained. Detachment could occur, either through adhesive break, i.e. at the

interface level or through cohesive break, i.e. within one of the two partners and very close to the interface (see Figure 2.7).

On this point, special emphasis must be laid on the particular case of concrete. Generally by cohesive break we mean a break in the glue joint because the substrate (the adherent) is more resistant than the adhesive. In case of concrete, it is very often the reverse, since this material has a very low skin strength. It can therefore be quickly deduced that gluing on concrete is impossible and unrealistic.

This rash statement must not be considered as an irrevocable condemnation. The question must be again addressed to the architect or the designer, so that constructive measures based on the mechanical properties of the glue can be proposed, such as functioning based on shear strength or by applying strains linked to gluing to a part of the structure made in high strength concrete. Gluing, like all innovative techniques in the case of concrete, requires imagination.

The significance of *safety* problems is totally different since these impart a subjective angle to the real technical obstacles, which brings us back to gluing as being culturally unacceptable. There are several problems.

First, let us think about testing: we do not know how to check the reality of a glue joint. We have destructive, discontinuous and heavy methods (coring) and non-destructive continuous methods that are not always very reliable (ultra-sound). It is clear that a lot more research has to be done into this problem. In this direction, establishing continuous testing methods could even lead to "smart gluing" ...

There is of course still a lot of work to be done to reach that point. Till then we sometimes have to use methods like clamping, developed to ensure that detached elements do not fall. But this is also a mistake: the addition of a mechanical attachment in the middle of a glued sheet makes us assume that we do not have faith in the gluing since the strain will get concentrated around the holes. This practice has meaning only if it is similar to a clamp meant to hold back the sheet in case of fatigue-driven detachment.

Resistance to fire is also a real problem, but this does not systematically condemn gluing. Joints are sensitive areas in case of fire. This is the reason why gluing is not generally allowed in tunnels and confined spaces. But this is not the case outside. There are two known solutions:

− cover the glued area through an anti-fire protective skin;

− use constructive measures to evacuate the heat flow before the temperature rises to prohibitive levels.

Here the rule is simple: reasoning should not take place on the material level but on the structure to be built.

These brief thoughts on the state of the art bring us directly to two questions: can gluing be considered presently as a reliable method of construction and, if so, which direction do we take to ensure its development?

To answer the first question, let us once again go through the *advantages of gluing*:

− it is a method of assembly where stress is distributed over a large surface, thus preventing local concentration and consequently incipient cracks;

− it is a technique which is relatively easy to use when mastered well; it can be cost-effective through reduction in implementation costs, since the raw material cost becomes of secondary importance on account of the small quantities of glue used;

− it is an alternative technique to the classical processes, which could encourage innovation or at least bring about competition between various technologies;

and *its disadvantages*:

− the method of construction must be suited for gluing (type and level of stress, and particularly condition of facing surfaces);

− temperature sensitivity of the glue must be taken into account, the operating temperature ranges must be specified, in order to define the type of glue to be used and provide special measures for protection against fire if necessary;

− the sensitivity of the adhesive to certain types of aging, such as fatigue of flexible structures subjected to vibrations.

This questioning invites us to go deeper into the gluing phenomenon. We then realize that lying concealed in the collective unconscious is a mixture of established observations and ready-made ideas [COG 00] like:

– gluing is not possible on greasy surfaces (which is not always true);

– the surface substratum must be treated (which is vague);

– the surface roughness and energy must be increased (rather more important are the processes of surface activation and other transformation);

– the joint must be correctly made (?);

– glue manufacturers must be consulted (yes of course, but not exclusively);

– tests must be carried out (which ones? the right choice must be made).

The following reflections will try to bring out some clarifications, but the debate certainly remains open.

5.1.2. *Definitions, reference points*

We mean by *glue* or *adhesive* any substance used to assemble bodies through interposition of their surfaces.

Gluing can then be described as a method of assembly of two solids with the help of a third body interposed between the two facing surfaces, called glue or adhesive.

The gluing technique is very old. Few examples can be given to prove this fact [MEY 74].

In Lower Egypt, remains of a wooden framework have been found, resin coated and with small flints originally stuck to form the teeth of a sickle. The object is dated to 4,500 B.C., i.e. at the end of prehistoric times in that region.

Stone engravings show that nearly 3,500 years ago, Egyptians used gluing for wood using Arabic gum (drawn from acacia gum trees) and other plant-based resins.

Phoenicians, Greeks and Romans used compounds with terebinth, beeswax or bitumen as bases to caulk boats.

We can say that the very first aeronautical usage of gluing – especially mythical – goes back to the story of the labyrinth of Minos in Crete: to escape from the maze, Deadalus and Icarus created wings which they glued with the help of wax. Following this, the young Icarus experienced the disastrous effect of the thermoplastic property of wax by going too close to the sun …

Glue was drawn by the Romans from mistletoe berries. When spread on a stand, the surface becomes sticky and can be used to catch birds who thus experience, at their own expense, gluing through contact.

It is only later that fish glue, bone glue and compounds based on milk casein made their appearance. However, this material hardly changed for centuries. Techniques, on the other hand, evolved. We can take for example the case of veneering with strong glue which saw its rise in the West in the 17th century leading to magnificent works of art which still exist today. The same applies to the gilding on glued surface. And these glues are still used at the time of epoxides.

The industrial evolution of glues took place based on two complementary influences:

– paper manufacturing is a big consumer of glue: in order to improve the competitiveness of firms in this sector, it was also necessary to create new development in the field of glue;

– the general development of chemistry, which has given rise to new possibilities in a technology which can be used for various purposes.

Here are some stages of this development for illustration purposes:

– the development of new products from existing basic material by using transformation methods relevant to traditional chemistry: water-based glue obtained by the dextrinization of starch, flour resins for making plywood panels, gummed kraft paper for packing and automatic labeling, rubber-based natural industrial glue ("rubber solution") or nitro-cellulose based glue (shoe industry);

– the appearance of the first synthetic resins: phenolics, used mainly in the wood industry, then urea formaldehyde;

– the increase in knowledge on adhesion, particularly regarding metals, the discovery and development of polyurethanes, followed by epoxides;

– consequences of the appearance of epoxy resins, which are related to the development of gluing under reduced pressure and structural gluing, the last technique being likely to replace the traditional assembly processes;

– gluing through fusion or thermogluing, which brings us back in some way to the Icarus myth …

Today the research undertaken in the areas of glue and gluing applied to civil engineering and construction in general follows two main directions:

– the assembly as such,

– the development of composite.

All the assembly techniques for construction materials are summarized in Table 5.1.

A closer look at this table surprises us, since gluing figures as the universal method of assembly while in reality, in a sector like the construction sector, it is far from being in a dominant position. This condition requires clarifications, which brings us directly to the theory adhesion. The subject cannot of course be fully dealt with here, but a few notions will be elaborated upon with the aim of helping the reader get into this complex problem, which has once again become relevant in today's construction world.

Material	Method of assembly	Observations
Wood	Spigot-and-fancet joint, dovetail Nailing, screwing Wedges	Associated most often to gluing (except for traditional framework)
	Gluing	
Stones Bricks Concrete blocks Mineral glass	Mortar Lead sheet Joint	(bonding or gluing?)
	Gluing	Repair of cracks Contraction joints Assembly of pre-fabricated parts
Fiber Fabric	Sewing, weaving, twisting Buttoning, hooking	
	Gluing	Needle punched carpet, for example
Plastic material	Welding (thermoplastic) Mechanical assemblies, screwing or associated systems	
	Gluing	Main method of assembly particularly for PVC
Metals	Welding — bead welding — point welding	Metallic assembly
	Screwing, bolting, riveting Swaging, clamping, bending	Mechanical assembly
	Gluing	Physico-chemical assembly?

Table 5.1. *Main assembly methods for materials*

5.1.3. *Adhesion and gluing: theoretical notions*

Adhesion is the phenomenon which creates adherence. It is therefore a concept of obvious significance but which cannot be measured directly. Its evaluation therefore depends on the purpose for which it is used. This explains why there are several theories based on different approaches but which are complementary. A very deep bibliographic summary carried out recently at LCPC by Huynh [HUY 00] uses the following classification:

– theory of *wettability*;

– *electrostatic* theory;

– *diffusion* theory;

– *chemical bond* theory;

– theory of *low diffusion interfacial layers*;

– *mechanical* theory.

These theories have been taken into account earlier by Favre [FAV 74]. It seems interesting to repeat his reasoning from an educational perspective. Let us add that what he referred to as the "physical approach" corresponded, apart from an exception, to the physico-chemical approach, which is the driving principle of this work. The exception in question concerns the mechanical theory which is rather similar to a macroscopic view of adhesion, while all other theories are based on microscopic view of the phenomenon.

5.1.3.1. *Theories of adhesion: physico-chemical approach*

In this approach we deal with adhesion in a more specifically molecular aspect (or the microscopic level), which brings into play all chemical bonds, whether these may be of low energy (Van der Waals bonds), medium energy (hydrogen bonds) or high energy (chemical bonds).

Van der Waals bonds consist of:

– the non-directional *dispersive forces* or London forces, of average energy W^d of the order of 5 kJ.mol^{-1} for equilibrium distances of the order of the nanometer; these apply particularly to non-polar polymers in contact with metal surfaces;

– the *induction or Debye forces*, due to the respective polarities of existing partners; non-dispersive, these apply particularly to polar polymers in contact with metal surfaces;

– the *dipole-dipole or Keesom interactions* which apply to the adhesion of polar polymers on surfaces susceptible of ionization.

To these forces, which are low in energy but non-negligible when they get accumulated on a significantly large surface, must be added the hydrogen bond interactions, of clearly higher energy (of the order of 20 kJ.mol^{-1} for equilibrium distances of 0.2 to 0.5 nm) which are directives and whose effect is globally equivalent to the previous one if present; we can still add II-bond, acid-base or electrostatic forces to be complete. We can then get the relationship expressing the adhesion energies stated above (referred to as Fowkes relationship [FOW 67]):

$$W_A = W_A^d + W_A^i + W_A^{dd} + W_A^H + W_A^\Pi + W_A^{ab} + W_A^e$$

where the first term is generally dominant. We can thus show that the accumulation of dispersive forces is sufficient to ensure adherence without having to make use of high energy chemical bonds.

The latter appear in the *theory of chemical bonds* which postulates the formation of very direct covalent bonds between the medium, and the adhesive. The energies that come into play are 10 to 100 times greater than those associated to the Van der Waals bonds for equilibrium distances of the order of the angström (1 to 2 Å i.e. 0.1 to 0.2 nm).

This theory has been developed particularly with respect to the adhesion of rubber on brass: sulfur used as vulcanizing agent for elastomers (see section 1.5) plays, with respect to copper, the role of a coupling agent (intermediate formation of copper sulfide followed by reaction with polyisoprene (Figure 5.1)).
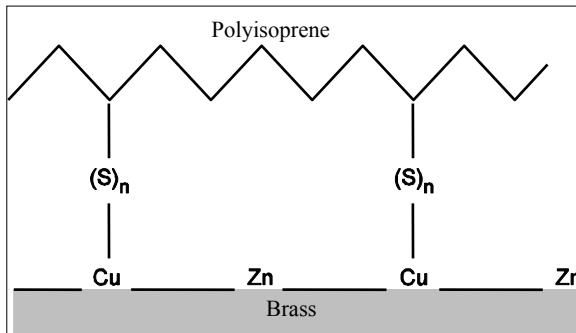
Figure 5.1. *Formation of covalent bond between brass and polyisoprene*

But its most important field of application is the use of organofunctional silanes on mineral surfaces and on various metals as activators for organic polymers (Table 5.2).

Of all the related mineral media, mineral glass occupies an important position. In the domain of construction we can give as example the sizing of fiberglass used as reinforcement in certain composites (see section 5.2.1). The active surface is then represented by the sites Si-O$^-$ or Si-OH whose affinity for organosilanes or organosiloxanes can be well imagined.

Name	Formula	Applications
Vinyl triethoxysilane	$CH_2 = CH - Si (O\ C_2H_5)_3$	Unsaturated polymers
γ methacryloxypropyl-trimethoxysilane	$CH_2 = C (CH_3)\ CO\ O - (CH_2)_3 - Si$ $(OCH_3)_3$	
γ glycidoxypropyl-trimethoxysilane	$CH_2 - CH - CH_2 - O - (CH_2)_3 - Si$ $(OCH_3)_3$ $\quad$ O	Most polymers
γ mercaptopropyl-trimethoxysilane	$HS - (CH_2)_3 - Si (OCH_3)_3$	
γ aminopropyl-triméthoxysilane	$H_2N - (CH_2)_3 - Si (OCH_3)_3$	Epoxy, phenolic, polyamides, polyurethane resins
n-β aminoethylamino-propyltrimethoxysilane	$H_2N - (CH_2)_2 - NH - (CH_2)_3 - Si$ $(OCH_3)_3$	

Table 5.2. *Silanes commonly used as adhesion activators for polymers on mineral or metallic surfaces (based on Plüddemann [PLU 70])*

The *electrostatic theory* is connected to the method of reasoning used previously. It assumes the existence of an electrical dual layer assimilating the bond to a flat capacitor. This was the idea of Deryaguin and Krotova [DER 48] who had noticed the emission of rapid electrons with significant energy (a few keV) when a contact was broken under vacuum.

Subsequent studies carried out to measure this electrostatic component of adhesion have shown that it could reach in some cases values comparable to the contribution of Van der Waals forces but this was quite rare. Thus it applies reasonably well to the copper-PMMA couple.

The *theory of diffusion* originated from the observation by Voyutskii [VOY 63] of the self-repair of rubber masses after incision. He considers diffusion to be the driving force of what he refers to the "autohesion" of rubber, i.e. their capacity to stick two surfaces to themselves when we press them one against the other.

He got interested in the interdiffusion of polymers in contact and the corresponding adhesion between the elements of the couple polymer1-polymer2 (which obviously includes autohesion). This implies that both the polymers are miscible and that therefore their solubility parameters are similar (see section 1.9.1).

This theory was completed by the introduction of the concept of creeping of polymeric chains [DEG 71] in a dummy tube [EDW 67] for analyzing the interpenetration kinetics of the chains for identical polymers placed in contact for time period less than the creep time [DEG 89].

This has no direct application to gluing, but it opens interesting perspectives for making new assemblies using this technique.

The *theory of low cohesion interfacial layers* was proposed by Bikerman [BIK 68] from the idea that the geometric interface, as a surface separating two bodies adhering to each other, has no physical reality strictly speaking: when we want to separate the substrate from the adhesive, the break takes place in an interfacial layer of low adhesion which in fact separates the substrate from the adhesive. He therefore defined seven possible classes of layers, which are as follows:

– the first class is the air which was not displaced from the surface of the substrate by the adhesive and forms a series of pores between the two stuck solids; the joint breaks when the fractures moves from one pore to the next. We can see here why wetting needs to be well executed;

– the second class includes zones that have low strength due to the presence of foreign bodies in the adhesive (pollution, additives etc.) which tend to accumulate at the interface during the curing of the adhesive;

– a third class which is similar to the previous one concerns the impurities initially present in the upper layer of the substrate and likely to cause weakness at the interface;

– the layers belonging to the fourth and fifth classes are a result of chemical reactions (oxidation, humidity) or physical reactions (adsorptions) between the atmosphere and the adhesive and medium respectively;

– the layers of the sixth and seventh classes bring into play on the one hand the reactive products of the adhesive and the substrate, of the two partners and of the medium on the other.

This classification may appear abstract and complex but it does have the advantages of analyzing the range of objects likely to intervene at the interface. It leads to the *concept of interphase* between the glued material, which assumes importance particularly when one of them itself is complex and with relatively low surface cohesion, as is the case for the standard hydraulic concrete.

Further, it highlights the *importance of wetting* while creating the interface. This is the important point which makes us realize the *deficiencies of the molecular approach* the way we discussed it.

All the interactions studied under this physico-chemical approach assumes equilibrium distances of the order of an angströms (or 0.1 of a nanometer). How can we in practical terms make a gluing between two real solid media by respecting such distances?

Let us consider the surface roughness obtained by various processes. We normally get:

- by turning or drilling :   0.4 to 6.3 μm   i.e.   4 000 to 63 000 Å
- by grinding: 0.1 to 1.6 μm   i.e.   1 000 to 16 000 Å
- by polishing: 0.05 to 0.4 μm   i.e.   500 to 4 000 Å

The proposed exercise amounts to, as proposed by Meynis de Paulin [MEY 74], attempting to place two chains of mountains, such as the Pyrenees and the Alps, opposite each other. Only the peaks in the rough patches will be in contact!

Salvation therefore came in the form of glue. *Wetting* of the glue on the substrate is a parameter up to now neglected, from its static and dynamic angles. We are once again confronted with the notions briefly dealt with in Chapter 2 on the aspect of the bitumen wetting the aggregate. This then leads us to look at the thermodynamic approach of adhesion.

5.1.3.2. *Theories of adhesion: thermodynamic approach*

The thermodynamic approach completes the purely physical view of the molecular theory which describes the forces involved and bond energies ensured through the notion of static and dynamic wetting. We therefore come back to the *theory of wetting,* which figures at the beginning of the classification adopted by Huynh.

We thus come back to the diagram in Figure 5.2 (which does not take into account the distortion of the solid at the drop edge and the resulting elastic force and thus ensures equilibrium in the vertical direction).
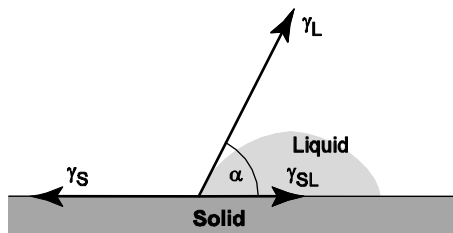

Figure 5.2. *Wetting of solid by a liquid. Definitions*

Wetting magnitude

Essentially, four parameters are considered.

The *contact angle* solid/liquid α, easy to measure, which is considered as the most significant empirical criterion to define the *wettability* of the studied solid by the considered liquid; we thus define for this solid substrate, wetting and non-wetting liquids (Figure 5.3).
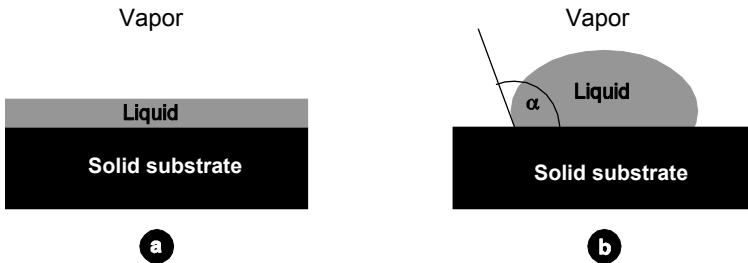

Figure 5.3. *Wetting liquid (a) and no-wetting liquid (b)*

The *surface tension of the liquid* γ_L, i.e. its aptitude to find the geometrical shape which will enable a given volume of this liquid to expand on the smallest possible surface.

Further, the work of cohesion required to increase the ds surface is expressed as:

$$dW_{cohesion} = \gamma_L \, ds$$

which implies that γ is measured J/m² (and more specifically in mJ/m²).

In addition, we have seen as far as molecular theory is concerned that it is possible to express γ_L as a function of the dispersive and non-dispersive forces which are exercised on the individual molecules as per the formula:

$$\gamma_L = \gamma_L^d + \gamma_L^{nd}$$

We can note that for water, the dispersive forces are essentially due to the hydrogen bonds, which are very intense to be specific, since their surface tension at 20°C is 79.7 mJ/m² while it is only 29.5 mJ/m² for benzene and 28.7 mJ/m² for ethanol.

We can now introduce the third parameter, the *surface tension of the solid* γ_S by going back to the expression proposed by Fowkes for work of adhesion but applied here to surface tension:

$$\gamma_S = \gamma_S^d + \gamma_S^i + \gamma_S^{dd} + \gamma_S^H + \gamma_S^\Pi + \gamma_S^{ab} + \gamma_S^e$$

Finally, we define *solid-liquid interfacial tension* γ_{SL} by extending surface tension where the second medium is compared to vacuum or more precisely to vapor in equilibrium with the liquid.

For this purpose, we can start by considering the case of two liquids (1 and 2) with the help of the Fowkes equation [FOW 67] modified by Tamai [TAM 67]:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d}$$

which becomes by analogy the case of a liquid and a solid:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S \gamma_L} - I_{SL}^{nd}$$

where the last term expresses the contribution of interactions due to non-dispersive constituents between the solid and the liquid.

Conditions of wettability

The equilibrium can be expressed by the Young equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \alpha$$

where γ_{LV} corresponds to γ_L (the liquid is in equilibrium with its vapor) and γ_{SV} is given by:

$$\gamma_{SV} = \gamma_S - \pi_e$$

where γ_S is the surface energy in vacuum and π_e is the spreading pressure due to vapor.

We can then deduce that: $\gamma_S = \gamma_{SL} + \gamma_L \cos \alpha + \pi_e$

However, there is a major difficulty in measuring γ_S. We must therefore go back to the expression for work of adhesion.

Work of adhesion

The solid-liquid *adhesion energy* (reversible) is defined by the Dupré equation:

$$W_A = \gamma_S + \gamma_L - \gamma_{SL}$$

which can be expressed by taking into account Young's formula:

$$W_A = \gamma_{LV} (1 + \cos \alpha) + \pi_e$$

and shows that the adhesion energy is maximum when the angle of contact α is nil.

The *cohesion energies* of the two partners involved can be expressed by equations of the type:

$$W_C = 2\gamma$$

which reflect the creation of two new interfaces in case of cohesive break. Generally, this term can be applied only to a liquid since the break of most classical bonds takes place in the adhesive or at the interface.

We can therefore introduce the spreading coefficient S which is equal to the difference between the adhesion energy and the cohesion energy, i.e.:

$$S = W_A - W_C$$

and becomes as per the Dupré formula:

$$S = \gamma_{SV} - \gamma_{SL} - \gamma_{LV}$$

We can therefore deduce that if the reversible energy of adhesion between liquid and solid W_A is greater than the cohesion energy W_C, spreading of the liquid is effective and:

$$\gamma_{SV} - \gamma_{SL} - \gamma_{LV} \geq 0$$

This result can be compared with Antonov's rule: the interfacial tension between two uniform solutions mutually saturated is equal to the difference in surface tensions of the two phases, an empirical law which can be extended to the solid-liquid interface and can then be expressed as:

$$\gamma_{SL} = \gamma_S - \gamma_L$$

We can therefore deduce that if the spreading coefficient S is positive, the vapor can be in equilibrium with the solid. A liquid film will always form between the solid and the vapor. The solid-vapor interface is in fact replaced by two interfaces, solid-liquid and liquid-vapor, which finally cancels out S.

This last result is not however always unanimous. We then use the notion of critical surface tension introduced by Zisman and Fox [FOX 52] with reference to the adhesiveness of bitumen as an important parameter. This term is explained here with respect to the overall context.

Critical surface tension

This concept was introduced to define the wettability of solids with low surface energies.

By measuring the contact angles of a homologous series of liquids placed on the same solid surface, we can obtain a linear relationship between the surface tension of the placed liquids and the cosine of the contact angle measure. An extrapolation of the straight line obtained at $\cos \alpha = 1$ (which corresponds to the perfect wetting) gives us the value of the critical surface tension γ_C below which the liquids wet perfectly the solid considered (Figure 5.4).
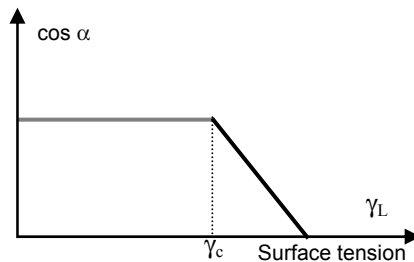

Figure 5.4. *Critical surface tension as per Zisman*

The straight line obtained through the Zisman method can be defined by the equation:

$$\cos \alpha = 1 + b \,(\gamma_C - \gamma_L)$$

where b is an empirical constant and γ_L the surface tension of the liquid.

Polymer	γ_C	Polymer	γ_C
Poly (1,1-dihydroperfluorooctyl-methacrylate)	10.6	Polyvinyl alcohol (PVAL)	37
		Polyvinyl acetate (PVAC)	37
Polyhexafluoropropylene	16.2	Poly methyl methacrylate (PMMA)	39
Polytetrafluoroethylene (PTFE)	18.5	Polyvinylchloride (PVC)	39
Polytrifluoroethylene	22	Polyvinylidene chloride (PVDC)	40
Polydimethylsiloxane	24	Polymethyl acrylate	41
Polyvinylidene fluoride (PVDF)	25	Polycarbonate (PC)	42
Polyvinyltrimethylsiloxane	25	Polyamide-6 (PA-6)	42
Polyvinyl fluoride (PVF)	28	Polyurethanes (PUR)	42-45
Polyvinylmethyl ether	29-30	Polyethylene terephtalate (PET)	43
Polypropylene (PP)	29	Eproxy resins (EP)	43-44
Polyethylene (LDPE)	31	Polyamide-11 (PA-11)	43
Polycholorotrifluoroethylene (PCTFE)	31	Polyacrylonitrile (PAN)	44
Propylene polyoxyde (PPOX)	32	Poly (1,4-cyclohexanedimethylene-terephtalate)	45
Polyacrylamide	33		
Polystyrene (PS)	33	Cellulose	45
Polyethylmethacrylate	33	Polyamide-6,6 (PA-6,6)	46
Polyethylacrylate	35	Resorcinol-formaldehyde resins	52
Cellulose acetate (CA)	36	Urea formaldehyde resins (UF)	61

Table 5.3. *Critical surface tensions γ_C (mJ.m^{-2} at 20 °C) of polymers, as per Lee [LEE 90]. The abbreviations of the main polymers used in civil engineering are indicated in brackets*

Based on this, Lee [LEE 90] proposed a classification of polymers depending on their wettability defined by their critical surface tension γ_C. He thus identified three classes (Table 5.3):

– *polymers with low wettability* ($\gamma_C < 30$ mJ.m^{-2}): most fluoride polymers, polysiloxanes and polyolefins, etc.;

– *polymers with medium wettability* ($30 < \gamma_C < 40$ mJ.m^{-2}): most vinyl polymers (polyvinyl acetates, polystyrenes, polyvinyl chlorides, polyethyle acrylate, polymethyl methacrylate, etc.);

– *polymers with high wettability* ($\gamma_C > 40$ mJ.m^{-2}): most polymers obtained through polycondensation (polycarbonates, polyesters, polyamides, EP, etc.).

The criterion of perfect wettability of a solid with low energy by a liquid with surface tension γ_L can then be expressed as:

$$\gamma_L < \gamma_C$$

Further, the Young equation becomes for cos $\alpha = 1$ or $\alpha = 0$ (perfect wettability):

$$\gamma_C = \gamma_S - \gamma^{\circ}_{SL} - \Pi^{\circ}_e$$

where γ°_{SL} is the interfacial tension solid-liquid when $\alpha = 0$ and Π°_e is the spreading pressure in the same case.

This means that the critical surface tension for a given solid is at the most equal to the surface tension of this solid.

From these general observations we can conclude that good adhesion requires an intimate contact between surfaces to be assembled and thus a good wettability of the adhesive on the medium. It refers here to a condition which is necessary but insufficient. This is reflected by striving for:

− γ_S *maximum*, which assumes the elimination of all surface pollution; this precaution is well-known to meticulous craftsmen and handymen; we can also think of surface treatment (see section. 4.3);

− γ_{SL} *minimum*, which depends essentially on the adhesive chosen, that is on the performance of glue formulators.

But obtaining a good wettability also depends on the manner of application. The *kinetics of wettability* will have to come into play to correctly grasp these phenomena. To this is added the *mechanical aspect of adhesion* which is placed at the macroscopic level in the entire theoretical research on the origin of adherence.

The pre-eminence of wettability does not however give it unanimity. Thus, Cognard [COG 00] does not consider wettability as a necessary condition, but as a favorable factor which should be combined with all the other interactions between the two surfaces.

5.1.3.3. *Kinetic aspect of adhesion*

Mainly, two parameters come into play during the spreading of the adhesive: roughness of the medium and viscosity of the applied liquid.

Substrate roughness is a complex factor.

From a macroscopic point of view, we understand that the peel strength of the bond between the adhesive and the substrate is improved if the substrate is slightly rough. We thus come to mechanical anchorage and it is the cohesion of the glue which is at stake.

In the same way, too much roughness can be dangerous since this does not allow very intimate contact between the spread out liquid (or the fluid mixture if it refers to a filled product) and the hollows of the substrate: the peaks will be wet while the troughs will not be in contact.

We will therefore strive for a moderate roughness and ensure that the hollows are wet.

It is interesting to note that the *mechanical theory* of adhesion stated at the beginning of this theoretical study is also based on the anchorage of the adhesive in the pores or between rough patches present on the surface of the solid. It was specially developed with respect to the adhesion of polymers on metals where the presence of oxides on the metal surface is used to increase adhesion.

The second parameter involved in the kinetics of wetting is the *viscosity of the adhesive.*

We have seen that wetting depends mainly on the wettability of the adhesive on the substrate. If wettability is very good, wetting can happen even with a highly viscous glue. In most cases when wettability is simply "good" it plays the role of a brake, which it is in essence, getting stronger with increasing size. Its role is therefore very significant.

The application of a bicomponent epoxy glue, i.e. a reactive resin, on a mineral substrate forms an interesting case [MOU 78]. Wetting is ensured by the constituents of the mixture, followed by the reaction between these with increase in viscosity and change into the solid state by retaining at the interface its initial properties.

The kinetics aspect of wetting includes the study of *hysteresis* linked to this phenomenon. We have already discussed this in Chapter 2 with respect to bitumen and will therefore not deal with the same once again. However, studies undertaken on the *dynamics of spreading in a drop of liquid on a solid surface* cannot be ignored.

We have seen that that the most significant criterion of wettability is the *contact angle* (Figure 4.3), which is easy to measure and helps to develop the theory of wettability in agreement with the experimental reality. However, the shape of the drop edge examined for measurement purposes is not strictly the shape of drops represented in Figure 4.4.

When a drop of liquid is placed on solid flat substrate, it can spread partially giving rise to a finite contact angle α_{equ} (partial wetting), or form a wet film (total

wetting). We have seen earlier that wettability can therefore be defined by the *coefficient of spreading* S expressed as:

$$S = \gamma_S - \gamma_{SL} - \gamma_L$$

and there are two possible cases.

The coefficient of spreading S is negative, wetting is partial and the contact angle α_{equ} is defined by:

$$\cos \alpha_{\acute{e}qu} = 1 + \frac{S}{\gamma_{LV}}$$

We can therefore see that the profile of the microscopic corner of the liquid film connecting to the solid is as is given in Figure 5.5.
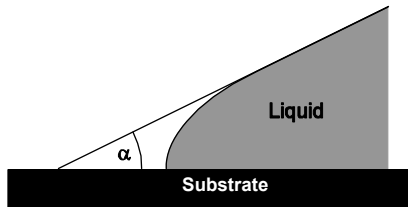
Figure 5.5. *Microscopic corner of a liquid film (based on Joanny [JOA 85])*

However, the profile of the drop itself (if it is relatively large) is as shown in Figure 5.6.
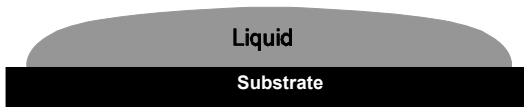
Figure 5.6. *Profile of the drop under dry spreading (based on De Gennes [DEG 90])*

The coefficient of spreading S is positive, the drops spreads fully but stops at low but finite thickness and the contact angle is practically nil.

For non-volatile liquids (polymers and heavy oils), the drop in equilibrium takes the shape of a pancake whose profile is the result of the equilibrium between the

forces of gravity, the long range forces and the forces represented by the coefficient of spreading.

If the liquid is volatile, in equilibrium with its vapor, a wet film appears covering the whole surfaces and which could eventually climb up a vertical wall up to very significant heights (several meters).

We have even observed a *precursor film* when a drop of liquid was spread on a dry medium, in front of the macroscopic face of the drop. This film, of lower thickness than the micrometer, which therefore cannot be seen with the naked eye, is due to the long range Van der Waals forces which have a tendency to thicken the liquid layer and become very significant in the corner bordering it (Figure 5.7).
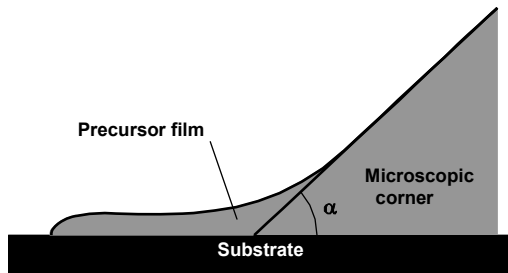

Figure 5.7. *Profile of a precursor film in front of a macroscopic corner (based on Joanny [JOA 85])*

As far as the *spreading of a drop of melted polymer on a solid surface*, is concerned, we can see formation of a macroscopic "foot" before the drop body. This is attributed to the sliding effect of the polymer on the solid surface because of the entanglements of the chains which is reflected by an extrapolated length at zero of the speeds profile (Figure 5.8).
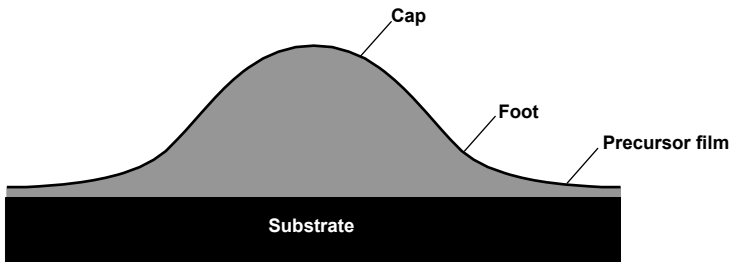

Figure 5.8. *Spreading of a drop of melted polymer on a solid surface (based on De Gennes [DEG 85])*

5.1.3.4. *Practical conclusions*

All the theoretical considerations made earlier have provided justification for the techniques practiced by glue users but these also bring to the fore some reflections which we will now dwell upon.

In the field of civil engineering which concerns us, we mainly look for *structural gluing*, that is, gluing likely to withstand a certain level of stress. We have already mentioned this term with respect to products for repairing concrete (section 3.1.1) but without really being more specific about its meaning.

The old French standard T 76-001 defined structural adhesive as an "Adhesive being involved in the whole structure, which could be subjected to a high percentage of its maximum load for a long period of time without any failure". No consensus could define the parameters underlying this definition. Consequently, the current European version (EN 923) confines its definition to the notion of structural jointing: "Jointing capable, as an integral part of a structure, to show a specific level of strength when subjected to a combination of stresses for a specified period". The adhesives which replace this function are rather defined on the basis of their chemical nature or their method of presentation.

The glues used, still referred to as *structural adhesives* (or adhesives of structure) as per the old terminology, belong essentially to one of the three chemical families which we have already seen: epoxy-amines, polyurethanes and acrylics (more specifically the derivatives of PMMA). These can therefore be called the *reactive adhesives* [COG 00], i.e. *in situ* reaction through polycondensation for the first two or chain polymerization for the third. In current practice, the most commonly used adhesives are the epoxy amines.

The action of these adhesives mainly involve two phenomena explained in the previous theoretical approach: wetting and mechanical anchorage.

Wetting should not be only considered from the static angle. We have realized the importance of its dynamic aspect which specifically involves the roughness of the support, an essential parameter of the mechanical approach and which explains why it must often be relayed by the application of a contact pressure to stimulate the movement of the glue film, even the mastic.

The effect of the support roughness highlights the complementary nature of the thermodynamic and mechanical approaches with the complex notion of wetting. This property encourages the interpenetration of the adhesive and the surface layers of the support but requires that the scale of roughness remains compatible with the

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overall viscosity of the glue, which puts forward the role of fillers eventually existing in the product.

Next to the structural adhesives, which we have just discussed, we should not forget the particular case of gluing of elastomers on metal stirrups for structure bearing systems. Here it is rather the theory of the chemical bond which is applied as seen in Figure 5.1, with of course another type of support.

In a general manner, these theoretical reflex ions can only be added to the wishes of the manufacturers regarding the care to be given for the preparation of the surfaces to be stuck and of the products to be used. It is up to the manufacturer to show their ingenuity to ensure that the users do not need to improvise much, while it is up to the users to attach the greatest importance to the recommendations of the manufacturers.

5.1.4. *Surface treatment*

The theoretical notions which have just been stated are in agreement with the rule book taught by glue professionals and craftsmen: to successfully execute an operation with this technique, we must start to work with clean surfaces. This elementary precaution (which is not always easy to perform) is nevertheless not sufficient; everything depends on the material to be glued. Furthermore there are cases where surface oxidation, for example, may improve adherence of the applied layer. We therefore come to the conclusion that surface treatment forms a part of a whole new world and that the subject cannot be dealt with in a few lines. We will therefore restrict ourselves to the experience acquired on this subject in the field of civil engineering.

As far as *gluing on steel* is concerned, experience specific to civil engineering is quite small. Does that mean that gluing holds no future in this field? Certainly not. We may feel that it could be an interesting alternative to welding which, as we know, can locally weaken the steel. It goes without saying that all welding cannot be replaced by gluing; this can be decided with the help of the resistance rating and the type of stress required, but there is a definite scope in this direction.

To these concerns can also be added the recommendations proposed for the maintenance of metal works by the application of paint as given in section 3.2.2.5. For processes specific to treatment of metal surfaces before gluing, the reader is advised to refer to specialized works [COG 00, SCH 92].

The problem pointed out for *gluing on concrete* is, however, original and is very much part of our scope.

The experience specific to civil engineering concentrates around the process of reinforcement or repair of structures through outside gluing of metal plates ("glued sheets") introduced by L'Hermite in the 1960s and which then went around the world. [LHE 67]. We will see further (section 4.2.3) how the appearance of carbon-epoxy composites on the market led to the evolution of the process by progressively removing the steel plates.

The low skin strength of concrete is the main difficulty encountered with respect to gluing on a concrete surface. Two paths can be explored:

– the use of glue as a local reinforcement binder, through impregnation of the surface and improvement of the interphase observed after gluing; this is the gamble of the process of L'Hermite;

– in new constructions, the use of high strength concrete which does not show skin weakness.

As before, we can associate with this problem – concrete surface treatment before gluing – the recommendations proposed with respect to products for repairing and for painting works in concrete structures in sections 3.1 and 3.2.3 respectively.

We could also mention *gluing of wood and gluing of plastics*, but here the experience specific to civil engineering is minimal and will increase as and when these materials take their places in the civil engineering field. For the time being, in the same way as gluing on steel, we request the reader to refer to specialized works (for example [COG 00]).

5.1.5. *Implementation: importance of "in situ cross-linking time"*

Let us proceed by analogy. When we analyze hydraulic concrete implementation, we can distinguish various phases: placing, waiting time which is in turn divided into phases:

– the dormant period;

– the setting;

– the hardening,

These phases are defined at the macroscopic level and we explain that the active principle of cohesion of the finished material, cement, intervenes through a set of complex chemical reactions, whose progress does not cover in a simple manner the phases defined above.

With the organic binders used for gluing, we can analyze in the same manner and define the following phases (without taking into account the prior operation of mixing, when dealing with a bicomponent):

– the glue application;

– the assembly;

followed by the waiting time consisting of:

– the setting;

– the curing.

Here we do not speak of the dormant period which is a term specific to cement setting, but on the whole the process takes place in the same manner. However, we should not make the mistake of pushing the analogy too far: it can be perfectly applied to certain bicomponent glues like epoxides where chemical reactions come into play, such as for cement, but for other types of glues, things are not as simple. We must come back to the method for implementing organic binders given in Table 1.1 where we distinguished:

– the monocomponents where implementation involves the transformation of the physical state of the product;

– the bicomponents where implementation involves chemical transformation of the glue.

For *monocomponents,* setting corresponds to:

– the evaporation of the solvent, for glues in solution;

– the emulsion failure followed by dewatering, for glues in emulsion or aqueous dispersion;

– rigidification through cooling for thermo fusible glues.

Since the assembly is done, there is no additional curing to wait for.

For *bicomponents* we again come across the two methods of polymer formation described in Chapter 1:

– polycondensation for epoxides and polyurethanes;

– chain polymerization for acrylics.

In the first case we observe a curing time, which we have referred to as *in situ cross-linking time* (see section 3.1.3.1), for products for repairing used on site, which is the time required for the chemical reaction to attain its state of equilibrium under conditions of temperature and pressure of the application. This time should not be ignored so as to ensure an assembly that is effective and long-lasting.

In the second case, the reaction is very rapid and the curing time is generally negligible. On the whole we consider the assembly to be done when the setting is effective.

5.1.6. *Principle adhesives used in civil engineering: notion of reversibility*

We have seen earlier that practically all glues currently used in civil engineering belong to the family of *epoxy resins* and more specifically to the epoxy-amine systems. What are the reasons for this type of exclusivity?

In the first place, it refers to *structural adhesives*, meant for assemblies capable of withstanding significant stress level during a significant period of time. These materials exhibit thermosetting behavior and their glass transition temperature is generally above 50 or else 60°C (if processing took place correctly of course). Thus, they are in the vitreous state at normal operating temperatures.

Their processing requires a certain minimum amount of care but is after all quite easy. However, qualified personnel is required.

Lastly we can vary at will the composition of this mixture (called "formulation") which could consist of, other than the polyepoxide base and the polyamine hardener, a plasticizer, a flexibilizer, a thixotropic agent (for use in verticals or under-surfaces), fillers, etc.

Among the polymer families existing on the market, we could think of using polyurethanes, acrylics (copolymers of PMMA) or the silicones. These products are seen in the building industry but rarely in civil engineering.

Lastly, a problem badly resolved by the epoxies but which may find practical answers in the next few years must be noted: how do you make a *reversible glue joint*?

The present-day realization that human constructions have a limited lifespan, that must be managed as such, has brought designers and decision-makers to also think about demolition, about dismantling and even "deconstruction", a neologism apt for the problem at hand. This operation comes with many forms of recovery, re-use and other recycling. Possibilities of detaching form part of the recovery methods which we would like to have at our disposal.

In more simple terms, to be able to restart an operation which was not entirely satisfactory is also a form of freedom which both the contractors as well as the craftsmen would like to possess.

The solution may come from the thermo fusible polymers, thermoplastics with high glass transition temperatures, a few instances of which have already been used in the building as well as other industrial sectors.

In conclusion, we could add that gluing can be a very useful and very effective assembly technique on the condition that it is incorporated in the general design of the structure to be constructed. If considered early enough, it could be an important factor for progress.

5.2. Organic matrix composite materials

Composite materials or more simply composites can be defined as materials resulting from the association of a continuous phase known as a matrix and a dispersed phase called strengthening, directed in a specific manner and mainly contributing mechanically. Thus wood may be considered as a natural example of a composite, lignin matrix strengthened with cellulose fiber.

5.2.1. *Constituents*

The matrix is meant to ensure the cohesion of the material on its whole, i.e.:

– to maintain the bond between the strengthening agent and their respective positions;

– to protect them with respect to the external environment: humidity, chemical attacks, abrasion and in that case, if it refers to a viscoelastic material such as in the case of organic polymers, to limit the risk of damage by the absorption of energy received and delayed restitution;

– to distribute stress and give the external shape to the part.

Matrices could be mineral (ceramic, mortar, concrete), metal (aluminium for example) or organic in nature. In the latter case, we can distinguish between flexible matrix composites (thermoplastic resins, elastomers, bitumen modified or not by polymers) and rigid matrix composites (thermosetting resins or thermosets; see section 1.4.1).

In everyday language, when we speak of composite without specifying the nature of the matrix, we generally refer to organic matrix composites [DAV 87].

The strengthening agent essentially plays a mechanical role. It brings rigidity and mechanical strength and can be set as per preferred orientation (it could be one, two or three dimensional as per the requirements of the planned structure).

The strengthening agents are essentially made up of fibers in the general sense of the term; long or short individual fibers, eventually forming a real framework. These could also be mineral in nature like fiberglass, or metal like concrete frames or even organic like polyacrylonitrile fibers. To latter may be added carbon fibers through their method of fabrication.

5.2.2. *General principles*

To strengthen, i.e. for improving the mechanical properties of the matrix, *the strengthening agent* must satisfy a certain number of criteria:
– its module must be clearly higher that the matrix module;
– it must be chemically inert with respect to the matrix.

On the other hand, *the matrix* must ensure the protection of the strengthening agent and its geometrical position in the structure. Lastly, it must create a strong bond (adhesion) between the two partners so that the transfer of stress from the matrix to the strengthening agent is ensured.

We can expect interesting properties from these materials – very light, high corrosion resistance, good thermal or sound insulation – and as far as their usage is concerned, very easy to process and great freedom of design on account of the shapes that they can assume.

Making a composite satisfying specific requirements demands the optimum selection of the basic constituents, matrix and strengthening agent. The process chosen must also respect the correct placing of strengthening agents as well as good impregnation of the fiber by the matrix so as to obtain optimal adhesion. This last property calls for a surface treatment of the fibers known as sizing.

5.2.3. *Basic material used*

5.2.3.1. *Strengthening agents*

We have seen previously that various types of strengthening agents are currently used: mineral fibers, organic fibers and carbon fibers.

Mineral fibers are essentially made up of *fiberglass*, produced by the extrusion of molten glass through a die in a platinum based alloy heated by the Joule effect, a large range of which is meant for the fabrication of composites.

Organic fibers appear mainly in the form of *aramide fibers* obtained from aromatic polyamides.

Carbon fibers are fabricated based on two main processes: from petroleum pitch or polyacrylonitrile (PAN). The most efficient products are made from yarn in PAN oxidized at 300°C and carbonized (1,500°C) under nitrogen; these are largely used for making high-performance composite.

Metal fibers (boron) and *ceramic fibers* (silicon carbide) also exist, but these do not have as of now any applications in the construction industry.

These different products figure systematically in Table 5.4.

Nature of fiber	Basic material	Quality	Module E (GPa)
Mineral	Glass	C ⟺ good chemical resistance	70
		D ⟺ good dielectric properties	50
		E ⟺ good electric properties	70
		R and S ⟺ high mechanical strength	85
Organic	Aromatic polyamide ("aramide")	standard	65
		high module	130
		new generation	≥ 140
Inorganic	Carbon	HR ⟺ high mechanical strength	230
		HM ⟺ high module	390
		THM ⟺ very high module	≥ 400

Table 5.4. *Main strengthening agents used in the construction industry*

5.2.3.2. *Conditioning of strengthening agents*

As per the type of strengthening required, we can condition the strengthening agents in different ways. In construction we mainly use *unidirectional forms*, i.e.:

– *the yarn* made-up of elementary parallel filaments, with or without torsion, continuous (very long) or cut (3 to 5 mm);

– *the roving or the mesh*, set of continuous and parallel filaments, without intentional torsion;

– *the strip*, made up of continuous yarn, placed in parallel side by side, defined by its width and weight per m²;

– *the unidirectional blanket* which is a very big strip.

There are also *surface forms*:

– *woven*, fabric or taffetas, satins, serges, high module fabric, uni-dimensional or multi-dimensional fabric (3D, 4D, as per the direction of the weave);

– *mats*, blankets of yarn, continuous or not, not woven, placed in a random manner in a plane.

There are also strengthening agents coated with resin in the viscous state, ready to use, called *preimpregnates,* which must be stored at low temperature and used strictly within the recommended time.

5.2.3.3. *Matrices*

We find two families of composites depending on whether the polymer which constitutes the matrix has a linear or cross-linked structure, i.e. with thermoplastic or thermorigid behavior.

For *thermoplastic matrices*, technology is presently evolving rapidly. Not very long ago, we mainly had polymers that were not very expensive, which gave products that could be used in a limited temperature range but which were easy to process. Certain varieties were very ductile with very good thermal properties (polyether sulfide and polyether ketone, for example). Their usage in civil engineering remained marginal.

Current research is directed towards high-module copolymers whose glass transition temperatures of the amorphous blocks is higher than the service temperature. It is nevertheless too early to consider them as material which is available for civil engineering.

The thermosetting matrices or resins possess mechanical and thermomechanical properties which are clearly superior when compared to the previous ones. These are

processed in the monomeric state, fluid, and their curing time depends on the polymerization reaction which comes into play.

Low temperature storage areas are required for using felt and fabric of preimpregnated fibers.

We can essentially see:

– unsaturated polymers (UPE) and their derivatives, vinylesters for example, which if strengthened by fiberglass can produce cheap material, which can be used in ambient temperature;

– the epoxy resins (EP) which possess superior mechanical, chemical and electrical properties when compared to the previous ones but of relatively higher price; they help to manufacture material that can be used up to 150 or 200°C.

As of now, these two families of resins are practically the only ones to be used in the construction industry.

We should also take note of:

– phenolic resins which possess low plasticity; these do not have very good mechanical properties but the material obtained from these can withstand temperatures up to 400°C; however, for health reasons, the likelihood of using this material remains very low (carcinogenic constituents);

– polyimide resins from which material usable at high temperatures (400°C) can be obtained but are particularly expensive;

– the melamine resins with similar mechanical properties as phenolic resins. Their electrical properties are interesting. They are not very flammable and are highly resistant to abrasion. These may be colored and used for making decorative and protective panels;

– silicon resins which are used for electrical insulation. Associated to fiberglass, these are used on account of their high heat resistance.

5.2.4. *Organic matrix composites and civil engineering*

In spite of the efforts made by their proponents, organic matrix composites still do not benefit from a significant growth for *construction* in civil engineering, mainly for two reasons: firstly their cost, which cannot be significantly reduced for large quantities keeping the present state of the technique in mind, and secondly the feedback on the durability of these composites is not sufficient enough to be able to carry out large scale implementations in civil engineering. Studies are underway for better understanding and for preparing for the future [ACM 96]. We can however

claim today that "organic matrix composites have all the assets to become innovative materials for the 21st century" [HAM 02].

The situation is nevertheless very favorable in the field of structure strengthening as we will see now.

5.2.4.1. *Repair and strengthening of structures*

We have seen previously that the L'Hermite process (see section 4.1.3) for gluing of metal sheets was commonly used for repairing and strengthening concrete structures. However, this technique had a disadvantage with respect to the weight of the sheets themselves: permanent overload for the structure, basic weight of the sheets to be handled and to be kept glued during and after processing, risk of accident in case of subsequent detachment. The appearance of high resistance composites has brought an alternative solution to this problem. We mainly consider composites of type carbon-epoxy: epoxy matrix and strengthening agent made of uni-directional or bi-directional carbon fibers. Gluing is ensured by an epoxy-amine adhesive adapted to the process which itself shows some variations:

– gluing of prefabricated *pultruded strips*, which can be handled like initial steel sheets but with greater ease;

– gluing of *dry fabric* in carbon fibers, the glue also playing the role of the composite matrix which is fabricated in situ from this fabric;

– use of *preimpregnates*, resin impregnated fabric and stored at low temperatures to block the reaction till the time of use, appearing in the form of rolls like adhesive tape. This process is not used very much in civil engineering in spite of its advantages of excellent impregnation of fibers by the matrix, due to the disadvantage of the necessity of storage in a cold room and prolonged heating after processing for cross-linking completion.

The first two processes, which both have advantages, are in fact complementary. [DAV 99]. We can state their overall advantages with respect to the metal sheets:

– lightness of the material which facilitates processing and does not require heavy scaffolding;

– insensitivity of the assembly to water (no corrosion).

Their size is however not a direct adaptation of the process making use of metal sheets, on account of their lightness which greatly changes their inertia. These questions, which require significant supportive feedback, explain the delay in regulations for officially formalizing this type of repair.

5.2.4.2. *Prevention of seismic risks*

A new application is in the process of being developed presently in Europe based on American and Japanese experiences in seismic areas: the *covering of bridge piers* by means of high strength flexible fiberglass for prevention of seismic risks.

It refers here to the increase in strength and ductility of load bearing structures to make them capable of absorbing sudden energy and to delay its effect. These are specific features of organic material which are used in this application, in addition to the overall strength brought by concrete.

The composite used in this type of application is again epoxy resin based, but the strengthening agent is not necessarily carbon fibers, with the aramide being sometimes preferred.

5.2.4.3. *Cables, stays, anchoring systems*

Another field where organic matrix composites have tried to bring about an original alternative solution is in the area of tight structures. This is how we have made on an experimental basis suspending cables strengthened with aramide fibers with high tensile strength, pre-stressing cables and even anchorage systems. This last application is interesting since anchorage still remains a worry for works managers. This however required meticulous research for fixing the anchorage: we had to avoid sliding without having to fold the fiber, a stress that it cannot bear.

Lastly, we can mention tight structures particularly new self-bearing entities called "tensegrity" [MOT 03], where this type of composite can play an important role.

5.3. Concrete admixtures

When we speak of organic material, we generally forget the role of discreet molecules which have proved to be indispensable in modern construction technology and which intervene through their physico-chemical properties or their mechanical properties. These refer to essentially concrete admixtures – air entraining agents, rheological admixtures (superplasticizers and derivatives) retarders, etc. – and *organics fibers* used in certain concrete or hydraulic mortar formulations. We also refer to these materials as *built-in* (*in cement matrices*). But more important are the admixtures.

Concrete is the base material for modern construction in developed societies. Everybody knows this but who can say what the concept of concrete holds? It is not enough to take a heap of stones and to sprinkle it with cement grout to obtain concrete. We will have to introduce the notion of the compactness of the aggregate structure and concretely consider the manner of obtaining a good packing. The processing associated to the physical, chemical and mechanical evolution of the initial mixture are an integral part of the definition of concrete.

We should also not forget that this generic term can also be applied to certain types of mixes, bituminous concretes as well as cement specific material. The problem does not exactly unfold in the same manner since both type of binders react differently from one another, but the starting point remains the same: *a good concrete is the result of good packing of the granular constituents*.

To obtain this effect, the mixture must be correctly lubricated. During the implementation of hydraulic concrete, the first idea is to increase the quantity of water, but then we come across another difficulty: the theory shows in fact that the quality of hardened concrete is better when the quantity of water used remains closest to the threshold necessary for the chemical reaction of cement, i.e. clearly less than what would be required to correctly handle the initial mixture ("fresh concrete"). This problem has been an obstacle for a long time to the development of high strength concrete. We can now claim to have solved this problem due to the arrival on the market and the development of new organic molecules which we will call *rheological admixtures*.

Another example: the hydraulic concretes call on a reactive binder, cement. Its reaction with water is exothermic and sensitive to temperature. In some cases (concreting of buried piles for example) processing can be disturbed by a too rapid setting and we may need a *retarder* for smooth processing. Some organic molecules can satisfy this requirement.

Lastly we can call on other admixtures which are organic in nature for specific uses like protection of concrete against frost (air entraining agents), projected concrete or mortar (water retaining agents, viscosity agents), even waterresisting (but here it refers more specifically to an application used in the building industry).

To finish the quick introduction, it seems appropriate to give some information regarding standardization and certification of these products by specifying that we must not confuse normative definition of functions and usage: one definition rests on tests concerning a given parameter, while usage normally involves several parameters at the same time. Thus we define the function of superplasticizers on the one hand and that of high range water reducers on the other while in practice we use the admixture as a superplasticizer as well as a high range water reducer.

Class	Desired effect (functions)	Base molecules
Water reducing/plasticizing admixture	Without modifying consistency, helps to reduce water content *(WR effect)* Without changing the water content increases the slump/spreading of the mixture *(P effect)* Helps to obtain both the effects at the same time	organic (essentially lignosulfonates and gluconates)
High range water reducing/superplasticizing admixture	Same effect as above but stronger: To highly reduce the water content *(HRE effect)* To considerably increase slumping/spreading *(SP effect)* Both the effects at the same time	organic (synthesis oligomers and polymers)
Water retaining admixture	Helps to reduce the loss of water by reducing bleeding	organic (polysaccharides)
Air entraining admixture	Helps to integrate during the mixing of a controlled quantity of fine voids spread evenly and which remain after hardening	organic (natural or synthetic)
Set accelerating admixture	Reduces time of start of transition of the mixture to pass from the plastic to the rigid state	minerals (ions)
Hardening accelerating admixture	Increases growth velocity of the initial strength of concrete, with or without change in the setting time	essentially minerals (ions)
Set retarding admixture	Increased time for start of transition of the mixture to pass from the plastic to the rigid state	organic and minerals
Water resisting admixture	Reduces the capillary absorption of the hardened concrete	organic salts and miscellaneous
Multipurpose admixture	Affects various properties of fresh or hardened concrete by ensuring more than one function defined above	

Table 5.5. *Classes of admixtures as per EN 934-2, with their chemical bases*

The European standard EN 934-2 proposes the following definition: "[an admixture for concrete is a] material added during the mixing process of concrete in a quantity not more than 5% by mass of the cement content of the concrete, to modify the properties of the mix in the fresh and/or hardened state." It then defines briefly various classes that we have incorporated in Table 5.5 by completing it with information on the nature of the major molecules which are used to formulate this product.

We can see from this table that the organic molecules are used to react on the rheoloy of fresh concrete (plasticizers, water reducers and their more effective counter parts) and the kinetics of setting (retarders), or for special effects (carrying calibrated voids to increase the resistance against frost, water retention for better cement hydration and avoiding bleeding or even improvement in the pore closure of concrete). Thus it covers the main area of the field of admixtures which we will study now.

Before we systematically present these materials, we would like to take a look to see the manner in which historically admixtures have asserted themselves in the technology of hydraulic concrete.

5.3.1. *The introduction of admixtures in concrete technology*

Binders from the cement family are said to be hydraulic because they set and perform their function with the help of chemical reactions of some of their constituents with water. Chemically, we consider that the water requirement of classical Portland cement corresponds to a value of the W/C (weight ratio of quantity of water to the quantity of cement in the mixture) of 0.33, i.e. 1/3 liter of water per kilogram of cement. Any concrete or mortar thus mixed displays a consistency of type "wet earth", not suitable for processing. We must reach approximately 0.6 to ensure that the mixture is perfectly fluid, but then the concrete obtained after hardening does not show high performance. In the minds of the classical user, the formulation of concrete remains the art of compromises.

The idea to introduce in the initial mixture ingredients which are organic in nature to make it more plastic has enjoyed varying fortunes (use of blood, for example), but has really become operational only with the specific use of derivatives of the paper pulp industry, the *lignosulfonates* (see Figure 5.9). Thus the first "plasticizers" were marketed in 1935. These have been used in a few civil engineering sites of that time but have really developed in Europe only after 1945. Let us add that the air entraining agents appeared in the USA in 1939 and reached Europe in 1947.

We can imagine the effects caused by the introduction of these "miracle products" in the construction market: contractors wondered whether what was proposed here was the result of a revolutionary technique or was just simply some "magical cure", the invention of chemists. In fact it was really a revolution.

It is curious to note how chemistry was isolated during those days in the world of civil engineering. There was in fact on one side mineral chemistry, a noble science, indispensable to cement manufacturers for developing concrete material which had great expectations, and on the other organic chemistry with tar and bitumen being its emblems, i.e. products marked with a strong sense of odor and with which we could easily get soiled. The idea of introducing organic products in concrete then appeared as a major sacrilege. Thus, for a long time, we could hear eminent specialists say that the best concrete could very well (and even should) do without admixtures or that admixtures were used only to save on cement. We can well imagine the controversy that developed from here … We were far from the present tendency where we finally recognize the complementary nature of all these products and materials and where we particularly consider admixtures as a fully-fledged constituent of concrete, or even cement since henceforth the delivery of cement with 1% admixtures is within European standards. Organic chemists thus had to accept an important challenge during that time and it required a lot of persistence on their part for them to be heard.

Briefly, we can say that recognizing the role of admixtures and particularly the most symbolic ones, those which we refer to as rheological admixtures, took place in three steps.

We have seen that the first product sold as plasticizers, the lignosulfonates, were *by-products* from the paper pulp industry. Other industries therefore became interested in this type of value addition and proposed bisulfitic "slop" and similar products, hoping to obtain interesting effects on a material which was quite tolerant in its composition, at least as seen by them. Unfortunately for these courageous innovators, the material in question did not always meet their expectations, even if these users then were not as demanding as today. Informed contractors quickly called researchers to their rescue to help them determine which of these proposals would lead them to the path of progress. We should note here that the French scientific and technical community played a pioneering role in this field: significant research work and work on regulations, carried out 1964 and 1985 by the various players concerned, producers and users in the large sense of the word, culminated in the establishment of a corpus of standards which would then serve as a base to the European standard EN 934 and to a national certification (NF make).

During this period, the environment changed inexorably: the notion of by-products was quickly replaced by the notion of *derived products*, i.e. developed for the use which was assigned to them but not yet specially manufactured for this purpose. Lignosulfonates, already mentioned earlier, appear in this category, but these had to be better refined in order to display better controlled properties. This requirement of quality control would later lead to the use of *gluconates*, synthetic molecules with effects similar to lignosulfonates. At the same time, users also started to consider these products as fully-fledged secondary materials, to be provided as such in the price specifications. The development of admixtures could finally take place.

We then reached the generalization of *synthetic products*. With their relatively early appearance, polynaphtalene sulfonates (PNS) and polymelamine sulfonates (PMS) were initially considered as high-end products, with their usage limited to important implementations, but later asserted themselves in construction and the "superplasticizers" class was specially created for them. Another contribution came more recently from the detergent industry: the search for new sequestering agents for Ca^{++} ions to soften water for washing led to the synthesis and the development of polycarboxylates polyethylenes (PCP) which could later be adapted to the problem of rheology of fresh concrete. These form the base of today's products and have enabled the production of new types of concrete which cannot be made without them. We can even state with respect to these that some of the molecules can be placed in the category of *nanomaterials* (see section 1.9.3).

5.3.2. *Rheological admixtures*

Admixtures which intervene in the rheology of fresh concrete have become during the course of time more and more significant, so much so that these can be considered today as fully-fledged constituents of concrete. Pumped concrete, hoisted to great heights, high strength concrete, very high strength concrete, self-leveling or self-placing and other types of special concrete could be designed only after rhenological admixtures were available and could thus prepare complicated mixtures, suited to each particular case, with the aim of attaining the expected performances. Our aim here is not to develop the theory of admixtures, particularly the theory of superplasticizers, but to just set out their principles and a broad outline. Several articles have appeared recently on this subject [RAM 98].

It is interesting to note in this respect that faced with the importance of the commercial stakes involved, literature (and communication in international symposiums, even those specialized on this subject) has remained for a long time confined to general aspects. The environment changed suddenly with the advent of

the impressive development of new generation superplasticizers. We then saw a flourish of publications which were singularly in constrast with the earlier literature.

5.3.2.1. *Plasticizers and their growth: mode of action*

We have seen that the first plasticizers, also called *water reducers,* to show that they can reduce the quantity of water required for obtaining an open mixture, were the *lignosulfonates*, by-products from the paper pulp manufacturing, which added value to lignin (Figure 5.9).
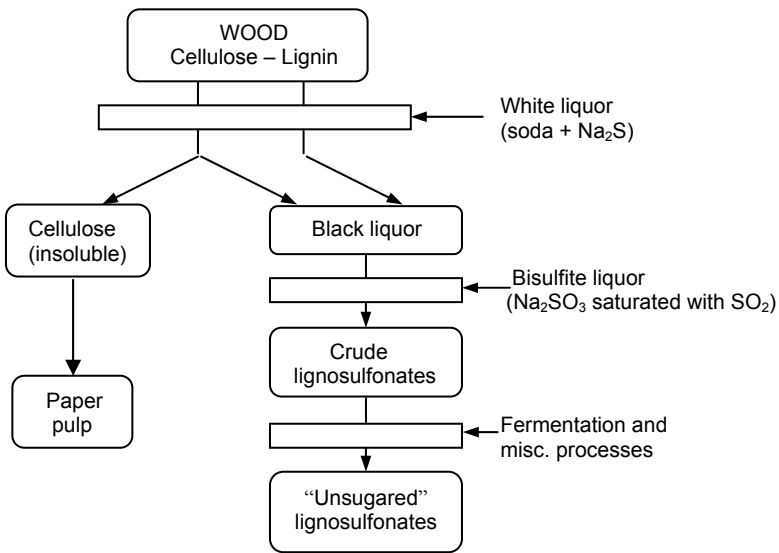

Figure 5.9. *Diagram of fabrication of lignosulfonates*

To interpret their mode of action [AIT 89, HUY 96, SPI 00] we should go back to the physico-chemical analysis of cement setting in concrete without admixtures.

It has been noted for a long time that cement grains in the mixture tend to flocculate, i.e. to form masses called "flocs" by electrostatic attraction. Moreover, these masses tend to trap a non-negligible quantity of water, thus reducing furthermore its availability for lubricating the mixture. The first studied effect is therefore the *deflocculation of cement grains*.

Lignosulfonates, strong acid salts, are negatively polarized and meet the requirement. We then put forward the electrostatic effect (Figure 5.10) which applies quite correctly to plasticizers and water reducers as well as all first generation superplasticizers (PNS and PMS). For gluconates, it is the complexation of ions, including aluminium, which comes into play giving a slight wetting effect.

The structures of these different molecules are outlined in Figure 5.11.
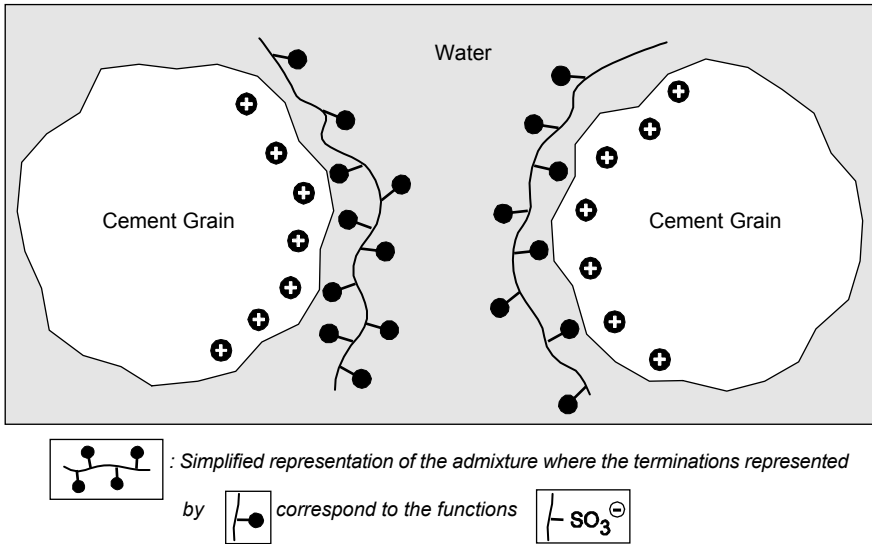

Figure 5.10. *Deflocculation through electrostatic effect. Simplified diagram which does not show the effect of the double ionic layer*

The *polynaphtalene sulfonates* (PNS) and the *polymelamine sulfonates* (PMS) are in reality oligomers obtained by polycondensation of formaldehyde HCH=O on naphthalene sulfonate or melamine sulfonate respectively in the presence of a bisulfite.

Lignosulfonates, however, quickly showed their limitations: a strong dose brings about considerable retarding effect on cement setting without at the same time allowing sufficient reduction of water to remove the excess, according to the quantity required for the chemical reaction of cement. Furthermore, they have demonstrated a certain air entraining effect and their natural origin display a certain vulnerability of structure, and thus efficiency.
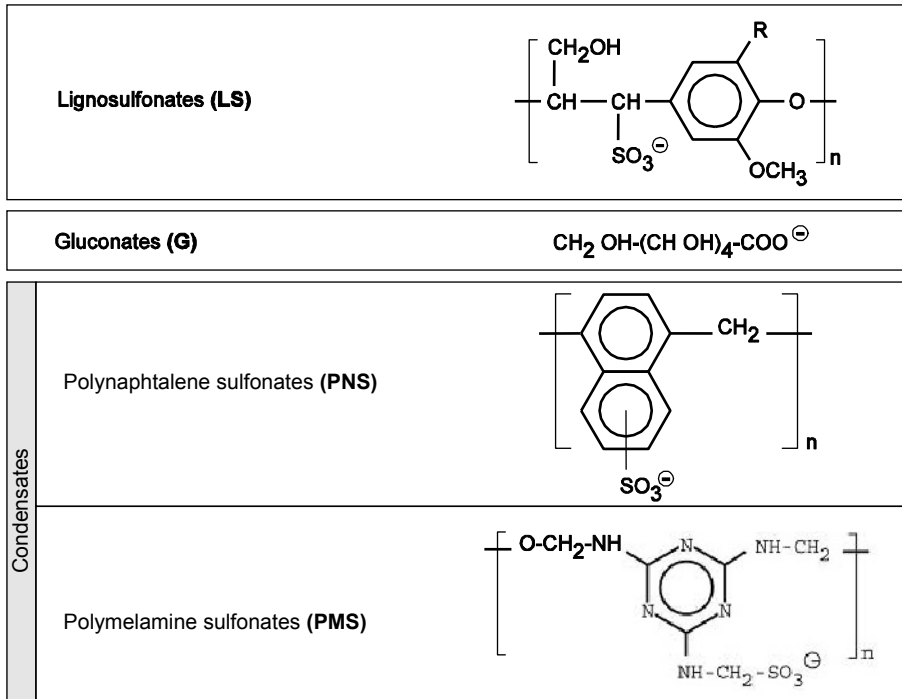
Lignosulfonates (LS)	
Gluconates (G)	$CH_2\,OH\text{-}(CH\,OH)_4\text{-}COO^{\ominus}$

Figure 5.11. *Schematic structures of classic plasticizers and superplasticizers*

As far as the retarding effect was concerned, it was quickly attributed to the sugars (pentoses and hexoses) present as impurities in the industrial lignosulfonates, but we had to admit that the purest forms of lignosulfonates themselves show a retarding effect due to a partial covering of the cement surfaces [MOU 72]. In fact both the effects are complementary.

The second aspect has greater consequence, which is derived from the tendency of lignosulfonates molecules to form a micro gel due to their strong anchorage and due to the presence of several hydrogen bonds. From this fact, they themselves consume water, their capacity for covering cement grains is greatly reduced and their efficiency is found to be limited. At the same time they can provoke a retarding effect (see section 5.3.3.1).

In spite of these disadvantages, lignosulfonates are still very useful as water reducer plasticizers since their cost price remains very attractive and we do not always require maximum performances. They are however more often replaced in

their field by gluconates – which show a similar chemical structure, with the OH groups and hydrogen bonds – whose regularity can be better ensured.

The appearance of the PMS on the market followed by PNS made it possible to go further: these do not demonstrate the effect of water retention like the lignosulfonates and further we noticed that by introducing the admixture at a later time, i.e. just before placing the concrete, we obtained results which were clearly better than the previous practices [PAI 90]. However, the method showed its limitations – mixing on site clearly produced lower quality than mixing in a concrete mixing plant – and we finally arrived at the compromise quite commonly used and which consists of 2/3 of the quantity of admixtures in the mixing plant and the addition of the remaining 1/3 on site. Concrete then becomes perfectly fluid and is easy to process.

Furthermore, we observed that these admixtures not only reacted through the electrostatic process, but that we had to also take into account the stereochemistry of their adsorption on the cement grains. In this way we arrived at the development of sulfonates, phosphonates and especially carboxylates with long chains which mainly react through the steric effect (Figure 5.12).
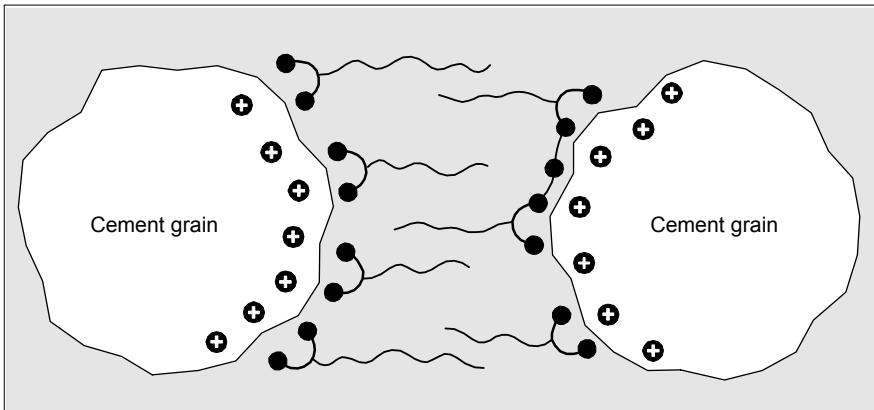

Figure 5.12. *Deflocculation and fluidization through steric effect*

On this basis we can easily see that chemists have enough material to expand the field of development of new admixtures, particularly by making use of *acrylic polymers* whose chemistry can exhibit its numerous possibilities.

It is interesting to note that these new products arrived just at the right time, to help concrete professionals escape from the increasing embarrassment of what we called at that time cement-admixture incompatibility. The French community had

even made it the theme of the National Project for concerted research between the different players of concrete constructions. This work helped to better define the problem, particularly with the help of a new test method which was validated in this framework [CAL 01].

The dream of the concrete manufacturer is to find the universal admixture, i.e. the product which works equally well with all types of cement. It is based on this principle, non-written but repeated many times, that admixtures were accepted by specialists when these appeared. This miracle product has of course never existed, but things worked out rather well insofar as the requirements of the constructers were not too numerous. Tolerances on the results were quite high and the notion of high strength concrete had still not entered the thought process. Each admixture manufacturer had a range of products for a given use and it was rare not to find the appropriate product for the specific work to be undertaken. We found differences between the advisability tests carried out in the laboratories and the reality on site six months later, but the professional knew how to manage this type of problem.

These ideal conditions did not stand up to several factors coming together which can be summarized in a well-known proverb: leave well alone. Even if the development of quality in the concrete industry contributed significantly to its progress, which it would be improper not to acknowledge, it also had adverse effects.

We spoke of tolerances on material properties: these could be reduced on account of better control of manufacturing parameters. On their side, cements had to evolve to match with the new European standards. From this point on, when an admixture showed a relatively pointed effect with the chosen cement, problems could arise.

Furthermore, the directives concerning environment protection brought in deep changes in the production of sand and aggregate. For example, water requirement for both alluvial material and broken rocks are not the same. We are not always masters of these parameters.

Finally, taking count of the previous limitations, certain parameters whose influence up to now had gone unnoticed appeared in the front row. Such was the case of temperature and role of fillers in the mixture.

For temperature we have noted the deviation between the advisability test and the site reality, which often occurs much later. The adjustment is not always easy since cement itself is a reactive product and thus changes. With all the precautions required, there still remains a certain uncertainty. This is why the method which consists in carrying out advisability tests and to follow the site with "the

equivalent mortar" of the considered concrete is a decisive progress vis-à-vis the stated problem. This method helps to work on the mortar after having set the parameters after a few tests on concrete.

Lastly we should not forget the role of fillers whose water consumption varies depending on their nature. We should know this characteristic to be able to integrate it in the setting parameters of the mixing plant.

5.3.2.2. *Perspectives*

As of now, plasticizers and superplasticizers which we have placed together under the term "rheological admixtures" represents a significant market since they have asserted themselves as indispensable constituents of concrete in civil engineering. We know relatively well their mode of action and can therefore make them evolve with full knowledge of the facts. Two questions remain however for today's chemists.

The first concerns specialists since the arrival of these products in the world of concrete: what does the admixture become in the hardened material? Does it play a mechanical role? Is it harmful to the environment?

At first glance this question seems of academic importance, at least for three reasons:
− the electrostatic and steric roles of the molecule in aqueous medium disappear when the concrete material has become a compact solid;
− the small doses used "drown" the organic molecules in the mass;
− the molecules, or rather the constituent ions of these products, are strongly attracted within the cement matrix through high energy electrovalent bonds, such that it is very difficult to extract them, particularly for analysis purposes, to check whether concrete has been correctly admixtured, for example …

We must not just be content with this, but must remain watchful with respect to this problem.

The second question is of more recent significance: are the admixtures in the concreting process aggressive on their environment and health in case of percolation into the water table?

These questions − and particularly the second one − have formed the subject matter of several studies today in most parts of developed countries. It does not question the technique of admixture but specifically concerns the research on new products.

5.3.3. *Other classes of admixture reacting on the rheology of fresh concrete*

Next to plasticizers and derivatives, we can classify set retarders into the category of admixtures with rheological characteristics – which can increase the time for placing by extending the time during which the mixture retains a handy consistency – and their antonyms the set accelerators on the one hand, and water retaining agents or viscosity agents on the other. However, the set accelerators and the hardening accelerators, which are products essentially based on specific mineral salts, will thus not be taken into account with respect to our study. Let us just mention that we sometimes find in the formulation of set accelerators, triethanolamine or a derivative of this organic base.

5.3.3.1. *Set retarders*

This class probably corresponds to the first use of an admixture in concrete even before the term or even the concept was defined. It is well known that the sugar – saccharose more precisely – is a powerful retarder which may even go up to provoking the complete stoppage of cement hydration in case of overdose. It is consequently prohibited French regulation for any utilization in prestressed concrete.

We have then used all sorts of molasses based by-products and other similar compounds, but the results were different and so random that the producers followed the same path for plasticizers. Thus, today's setting retarders are manufactured essentially based on pure sugars, gluconates (and eventually lignosulfonates) to obtain at the same time a plasticizing effect. We also come across derivatives of phosphorus, phosphates and phosphonates.

We generally consider that the retarding effect is due to the excess covering of cement grains with admixture molecules, which disturbs the penetration of the water molecules, retards hydration and therefore the setting. The presence of the OH groups in these molecules reinforces the membrane effect by forming hydrogen bonds which act as water retentive agents.

Retarders are used particulalry for concreting buried piles – their containment does not allow the discharge of heat due to cement hydration from escaping – and works carried out in hot weather.

5.3.3.2. *Water retaining agents*

These products are defined by the standard as agents meant to reduce bleeding and the segregation that follows. This is the effect sought after in self-placing or self-leveling of concretes where they are considered as formulation *stabilizers*. But in civil engineering these admixtures are specially used in the technique of projected concrete. These are then meant to trap the water required for hydration of cement

during the projection phase and the anchorage of the mixture on the face which must receive it. Since this water retention is accompanied by an increase in the viscosity of the slurry, they are also called *viscosity agents*.

The formulations used are of two types: mineral or organic. The latter are essentially polysaccharide-based consisting of a number of OH groups likely to retain the water molecule through the hydrogen bond.

5.3.4. *Other admixtures and connected products organic in nature*

If processing problems are the source for obtaining high-performance concrete, that does not necessarily mean durability, particularly with respect to environmental aggression due to water, i.e. mainly frost. Furthermore, during the first few hours after placing, i.e. during the phase of cement hydration, concrete can be subjected to the effect of too rapid evaporation of water or micro cracking on account of shrinkage. We can then easily use water repellents and air entraining agents, which are strictly admixtures on the one hand and curing compounds and organic fibers which can be associated with them on the other.

5.3.4.1. *Water resisting admixtures*

Defined as admixtures meant to reduce capillary absorption of hardened concrete, these products are not very often used in large structures where the concrete used in general are of high strength and thus very closed. They can however be very useful in the building field where we use traditional concrete which is more sensitive to humidity.

The formulations used are generally stearate-based or based on molecules with similar structure. We also come across paraffin emulsions.

5.3.4.2. *Air entraining agents*

This odd term is associated – in an unexpected manner for a layman – to the protection of concrete against gel.

Hydraulic concrete is a porous material, which is generally found outdoors, therefore subjected to the action of water and temperature variations at the same time. In case of intense frost, a classical concrete has a tendency to behave like a porous frost sensitive rock i.e. to crack in a random manner. This tendency is slowed down if particular care was taken during production and if compactness was sufficient. The diameter of the capillaries is too small for water to travel, but the optimum is obviously not obtained everywhere and there is still a long way to go.

The idea was then to provide for this effect by provoking the creation of a network of voids within the concrete with the help of surface active agents used during mixing. Its origin was the accidental discovery, during the end of the 1930s, of a pavement concrete particularly resistant to frost, where cement was lubricated with grease and soap used as grinding agent [LAW 39, quoted by RIV 95].

M. Pigeon – who devoted quite a few years with his team to the study of air entraining agents, which earned him the name of "Dr Bubble" – reminds us that several often contradictory theories have been put forward to interpret the way these micro bubbles act. These bring into play the hydraulic pressure in capillaries, the osmotic pressure and surface tensions. We generally consider that the bubbles act as an expansion tank for water and avoids the formation of a network of capillaries large enough to be able to move over long distances [PIG 88], [PIG 95].

The efficiency of the product can be seen in the size and the distribution of the voids, which can be analyzed based on a microscopic test on a test specimen of hardened concrete (for a minimum of seven days), which help to particularly determine the spacing factor $\bar{L}$. The values retained by the standard (EN 934-2) correspond to $\bar{L} < 0.2$ mm with an air content in fresh concrete between 4 and 6% in volume.

The first products used industrially to generate these voids were plant based ("vinsol" resins drawn from roots of the Oregon cedar) but other types of products were also used, from animal bases and specially from petroleum bases, which have given rise to the manufacturing of synthetic products of more controlled quality like alkylarylsulfonates, surface active agents of type anion-active. Both the types of products continue to be used, but there is a clear favorable tendency for the development of synthetic products, to satisfy at the same time the requirements of quality and compatibility with the different constituents, both major and more so minor constituents of concrete.

The main difficulty encountered with these products is the reduction in strength due to the increase in voids (Feret's Law) which must be perfectly controlled when dealing with large structures, for example. We also consider that the introduction of 1% air reduces the strength by 5%. This particularly implies the simultaneous use of superplasticizer compatible with the air entraining agent and in right quantities. Furthermore, the stability of voids during the cement hydration phase remains a worry for admixture formulators. Fundamental studies on this subject bring into play the very complex and very expensive means of analysis: electronic microscopes with scanning, environmental microscopes, etc. If we add to this the fact that the quantities of these products used are so low that at the end of the chain, the production tonnage is very low, we understand why producers are not inclined to invest in new research this area. However, it remains that protection of concrete

against the effects of frost is a definite concern for countries experiencing this kind of climatic effect.

5.3.4.3. *Curing compounds*

The most delicate phase of hydraulic concrete setting is during the first few hours, when the water-cement mixture reacts. It is therefore important that the water necessary for the reaction, does not leave the system. Technically, it is a source for concern when setting takes place outdoors since the mixture is subjected to the action of heat created by hydration, the wind or just the atmospheric conditions when hygrometry is low.

There various methods could have been used for safeguarding fresh concrete from drying – regular spraying, covering even with wet straw – but for processing large surfaces like highway slabs, we have developed a process which consists in covering the concrete through the projection of a *curing compound* which is very simply a type of paint with temporary effect. Later, its use spread to processing of all structures in concrete.

This temporary effect brings forth questions which are difficult to answer since we need the film to form as soon as possible on the fresh concrete surface since the effect required takes place particularly during the first few hours (for effectiveness) and after concrete hardening it must as disappear quickly (for brushability). For pavements where road markings are required, we use the degradation of the film by the sun's rays associated to the first effects of traffic, but for structures which must be covered by a damp-proof membrane (see section 4.1.1), we have to use brushing. Both the requirements are somewhat contradictory.

As of now, efficiency is considered to be a determining factor as per French regulations and placed at a relatively higher level. From this fact, products which meet these requirements are formulations in the solvent phase since no emulsion could cross the barrier of the efficiency test.

We can observe here that the test in question consists of measuring the loss of water from a test specimen protected by the product after being exposed to infrared rays in an oven. The test specimen used consists mainly of a concrete slab of large size ($40 \times 40 \times 10 \text{ cm}^3$) directly resulting from studies carried out in the laboratory while constructing concrete roads. The equipment used is a high precision weighing device taking into account the small loss for a large quantity. Furthermore, the test was carried out on three test specimens at the same time. This required three weighing devices and considerable investment when compared to the targeted market. When it was time to make a European standard, a long study had to be

carried out within a European team to reduce the size of the test specimen by retaining at the same time the representative nature of the test.

5.3.4.4. *Organic fibers*

Shrinkage of concrete in its raw form in the plastic phase can be controlled by adding polypropylene fibers with high molecular weight, hot extruded and cold drawn, 1 cm in length and with a diameter of around 10 μm [BUY 02].

We can see that the polypropylene fibers have a favorable effect on the increase in strength of the raw mortar and can replace the welded mesh used to restrict corresponding cracking. On the contrary, the fibers do not significantly influence long-term shrinking and must evidently not be considered as hardened concrete armoring.

Another interesting and unexpected effect can be obtained with this material: polypropylene, existing in concrete walls of tunnels, can retard the effects of fire in concrete. We have in fact noted that if the fibers are dispersed correctly and if the overall performances required from the concrete are not very significant, the heat can melt the fibers which enter the cracks and the capillaries of the concrete, create canals and encourage the escape of water vapor, thus avoiding the concrete from spalling.

5.4. General conclusions

Two aspects of organic material considered as cohesion admixtures were dealt in this chapter.

The first concerns adhesive bonding or gluing, general adhesion and an interesting associated application, the formulation of organic matrix composites. The second is centered around concrete admixtures. We can try to remember a few general ideas.

The study of *gluing* is quite disconcerting. Theories and techniques of gluing often display divergences which are difficult to surmount. There remains a lot of work to be done in this field. It is not a sufficient reason to ignore or abandon this type of construction technique but there is still a long way to go. We could however state that the *development of gluing in construction must not be left to the specialists; it concerns all,* designers, architects, engineers, multi-disciplinary researchers including those in life sciences. We must aim at a global design.

Organic matrix composites, the material of the future, is being developed in the civil engineering field but has still not given rise to significant works in the physico-

chemical arena. Their introduction is too recent for possible problems to arise that require in-depth structural studies outside the laboratory of producers.

Today *admixtures* have become a separate constituent of concrete. The essential part of production concerns the rheological admixtures as such – plasticizers, water reducers and their higher counterparts superplasticizers and high range water reducers – but the other types of admixtures have also become common. Concrete formula used in all the large sites and all mixing plants can no longer do without the range of admixtures proposed by the corresponding profession. This comes from the progress brought forward by new products along with the requirements of the user, the evolution in the quality of the aggregate available and better knowledge on the way they act.