CBL RAPPORT NR. 40

DENSIFIED CEMENT ULTRA-FINE PARTICLE-BASED MATERIALS

by

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Bache H H 1981 Densified cementlultrafine particle-based materials Paper presented at 2nd Int. Con5 on Superplasticizers in Concrete, Ottawa, Canada, 10-12 June, 1981 (Available as CBL Report No 40 from Aalborg Portland, PO Box 165, DK-9100, Aalborg, Denmark)

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Abstract

This paper describes a new class of materials with binders of densely packed cement and ultra-fine particles arranged in the spaces between the cement. The new materials are shaped from a viscous mass in a low stress field - in spite of an extremely low water content (0.13 - 0.18 by weight of cement + ultra-fine particles). The dense packing is achieved by using a large quantity of superplasticizer.
Concrete made with the new binder is far more durable than ordinary concrete and has a 3-5 times higher compressive strength than this (120-270 MPa). The geometric, kinematic and dynamic principles for arranging the fine particles in a dense structure are discussed, with special reference to the role of dispersing agents. The chapters on the hardened material and applications concentrate mainly on the principles for developing new composite materials and structures that combine the excellent properties of the new binder with properties which this does not possess, for example, high tensile strength and ductility.

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Introduction

This paper describes a new type of cement-based materials that are 3-5 times stronger than concrete and far more durable than this.*
Production of the new materials is made possible by superplasticizers, which change flocculent fine-particle systems of cement and silica fume (average diameter about 0.1 μ) to systems that can be densely packed in a low-stress field and with a very low water content. The paper is intended to give a picture of the basic principles of the construction of these materials and their uses. Only such specific factors (data etc.) as are considered necessary for this purpose are mentioned. Since the principles involved are of a universal nature and deal mainly with matters relating to overcoming locking surface forces between particles and the behaviour of hardened materials based on strong, brittle binders, it is my hope that the paper may also help towards an increased understanding of superplasticized concrete in general.

**The materials have been developed by the Danish cement producer, Aktieselskabet Aalborg Portland-Cement-Fabrik and are marketed under the trade name* DENSIT ®

Contents

1 General principles

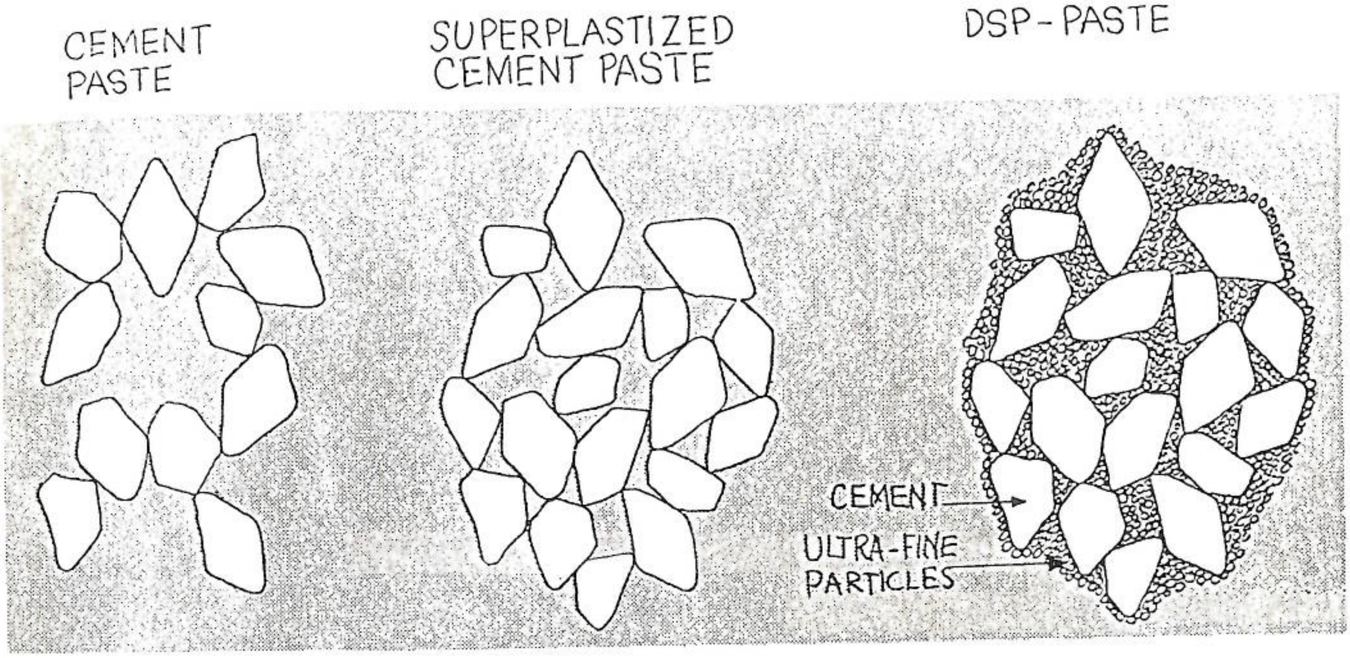


Fig. 1.1. The structure of the paste in fresh concrete based on 1) Portland Cement 2) Portland Cement + a superplasticizer and 3) Portland Cement + silica fume + a superplasticizer.

Densified cement/ultra-fine particle-based materials belong to a new class of materials defined as materials with a matrix comprising, or formed from, 1) densely packed particles of a size ranging from 0.5 to 100 μ, and 2) homogeneously arranged, ultra-fine particles ranging in size from about 50 Å to 0.5 μ, arranged in the spaces between the larger particles.

The shaping of the fresh material is typically performed from a viscous mass in a low stress field achieved by eliminating the locking effect of surface forces between adjacent particles by means of dispersing agents.

For the sake of brevity, the new materials are termed DSP, referring to »*Densified Systems containing homogeneously arranged, ultra-fine Particles*«. In the actual context, the densely packed particles are normally Portland cement, and the ultra-fine particles silica fume. In a more general context, the densified cement/ultra-fine, particle-based materials would be termed »*Cement-silica-based DSP*«, but in this paper, which deals only with cement-based materials, the shorter term »*DSP*« refers to cement-based DSP.

The structure of the fresh paste is shown in FIG 1.1, in which it is compared with that of ordinary cement paste and superplasticized cement paste.

The principal characteristics of DSP-materials are as follows:

1) The new materials allow geometric and kinematic principles for arranging larger bodies in a desired configuration - in particular, in a very dense arrangement - to be applied to fine-particle systems, which has not hitherto been possible owing to locking surface forces.

2) The fresh material has high internal coherence, permitting shaping without liquid being squeezed out, i.e., with no bleeding, even in the most fluid material.

3) Due to the very dense hardened structure, the strength and durability are very much increased compared with ordinary cement-based materials.

Mechanical fixation of fine, incorporated fibres is increased even more due to the fact that the dimensions of roughness and wave configuration of the fibres which are necessary for obtaining »mechanical locking« in the matrix are reduced to about 1/100. This makes it possible to achieve »mechanical locking« of fibres that are one to two orders of magnitude finer than the fibres that could hitherto be »mechanically locked«.

2 Background

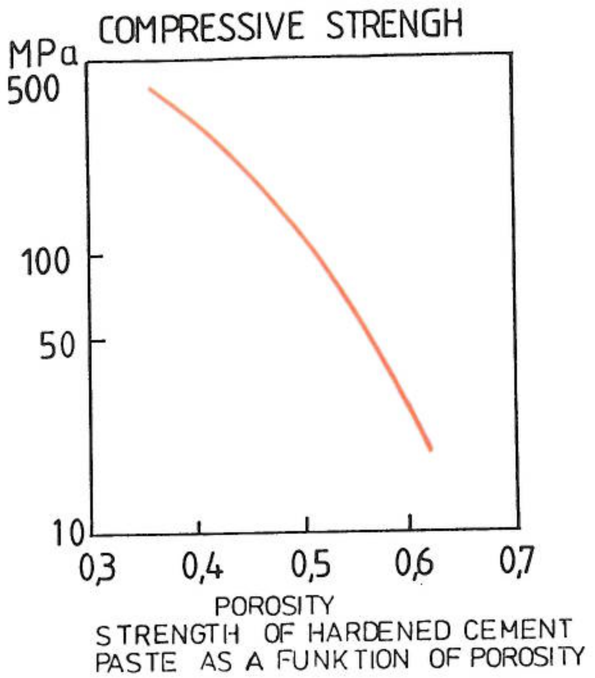


Fig. 2.1. Relationship between compressive strength and porosity of hardened cement paste. The experiments were carried out with small cylindrical specimens (volume 1 cm³) made by vibro-pressing with oscillating pressure up to 10 MPa for the densest specimens. For normal quality concrete, the porosity of the cement paste is about 0.6-0.5, corresponding to a water/cement ratio of 0.5-0.3 by weight.
In the experiments, considerably heavier compaction was used than in normal concrete production, resulting in paste strengths of up to 350 MPa. This strength is 5-10 times higher than the strength of the cement paste binding sand and stone in ordinary concrete.
The porosity mentioned is the porosity of the cement powder prior to hydration. [1]

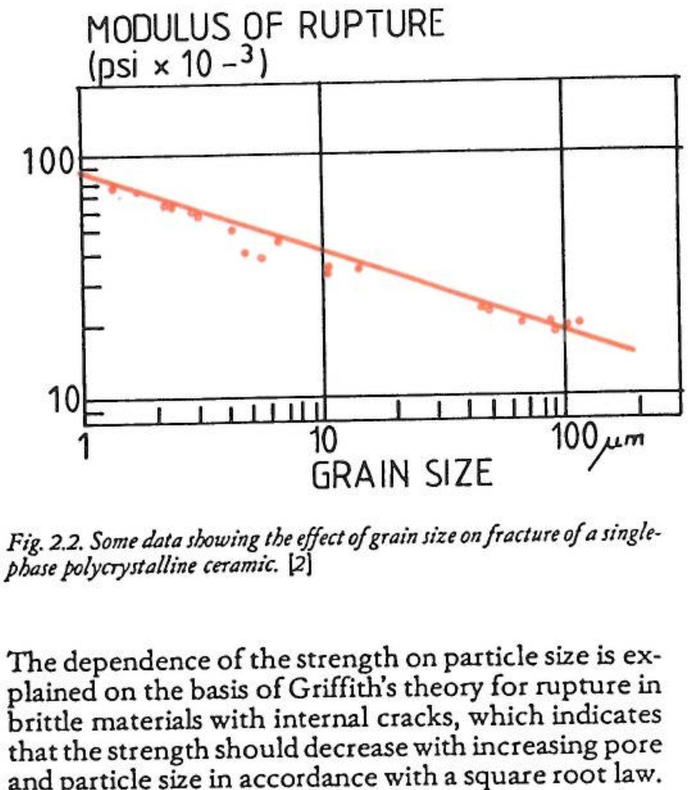


Fig. 2.2. Some data showing the effect of grain size on fracture of a single-phase polycrystalline ceramic. [2]

The traditional development of high-strength concrete has had a single aim: to reduce the porosity of the cement paste.
On account of attractive surface forces between adjacent cement particles in ordinary, unsuperplasticized paste, the particles are locked in a relatively open structure as shown in FIG 1.1.
This previously limited the quality of concrete made by the ordinary soft-casting method, corresponding to a compressive strength of about 60 MPa.

2.1 Mechanical compaction

Only by using heavy mechanical compaction was it possible to overcome the locking surface forces and pack the cement as densely as permitted by the particle geometry - typically corresponding to a water/cement ratio of about 0.2 - resulting in very high strengths, as illustrated in FIG 2.1.
One important means of achieving even higher strength is to use finer particles (cement), provided the low porosity can be retained. This approach has not attracted a great deal of interest in the field of concrete, although it has long since been used in other fields.
Thus, Kingery [2] showed that the strength of single-phase polycrystalline ceramic materials increased with reduced particle dimension as shown in FIG 2.2.

The dependence of the strength on particle size is explained on the basis of Griffith's theory for rupture in brittle materials with internal cracks, which indicates that the strength should decrease with increasing pore and particle size in accordance with a square root law. In the case of densely packed cement with a very low water/cement ratio, we must expect a structure to be formed that is very similar to the sintered particle structure mentioned by Kingery; this makes the use of very fine cement in connection with dense structures particularly interesting.

2.2 Superplasticizers

The development of effective agents for dispersing Portland cement in water - the so-called »concrete superplasticizers« represented a tremendous advance in the production of high quality concrete.
It became possible to make concrete with densely arranged cement using traditional soft-casting methods. In the last 10 years, soft-cast, high-quality concrete has been produced with water/cement ratios of about 0.25 and compressive strengths of more than 100 MPa. For example, Hattory [3] mentions soft-cast, superplasticized concrete cured in water at 20° C for one year, with a compressive strength of 120.6 MPa (water/cement ratio 0.25).

2.3 Cement particle size and particle size distribution

In 1973, Bache [4] suggested that the quality of superplasticized concrete could be improved still further by adjusting the particle size (part of the cement being extremely fine) and the particle size distribution of the cement.

This prediction was based on the experience regarding increased strength of ceramics with reduced particle size and the application of geometrical principles regarding the achievement of great density by special gap-grading on the assumption that the superplasticizers would be able to disperse very fine cement efficiently.

Experimental work on superplasticized concrete, combining ordinary cement and very fine cement to obtain high-quality materials, as predicted above, was started at the Cement and Concrete Laboratory of Aalborg Portland at the beginning of 1978.

2.4 Silica fume and the first DSP-concrete

During this work we became familiar with silica fume*, which consists of spherical particles with an average diameter of 0.1 μ, i.e. 1/50-1/100 that of the cement.

A combination of densely packed cement and silica was found preferable to graded cement for several reasons:

1) The silica particles are smaller than even the finest cement we can produce by grinding and are therefore more conducive to dense packing into the spaces between the cement particles.

2) The silica particles, being formed by condensation from gas phase, are spherical in shape (unlike crushed cement particles, which are angular). This makes the silica particles even more suitable for dense packing than very fine cement.

3) The particles are chemically less reactive than cement, which eliminates the problem of too rapid hardening encountered with very fine cement; in addition, the silica is likely to ensure the formation of a coherent structural skeleton between the cement particles, resulting in a fine, dense micro-structure (very fine cement is likely to dissolve too quickly for this purpose).

The exciting question was whether superplasticizers would be able to disperse the ultra-fine silica powder together with Portland cement.

Nature showed herself from her best side from the very first experiments in May 1978, by confirming the predictions regarding very low water requirement and high strength of the hardened material.

*Silica fume is a waste product from ferro-silicium production; it has actually been used in ordinary concrete for more than 30 years [5].

3 Structure and properties of fresh material

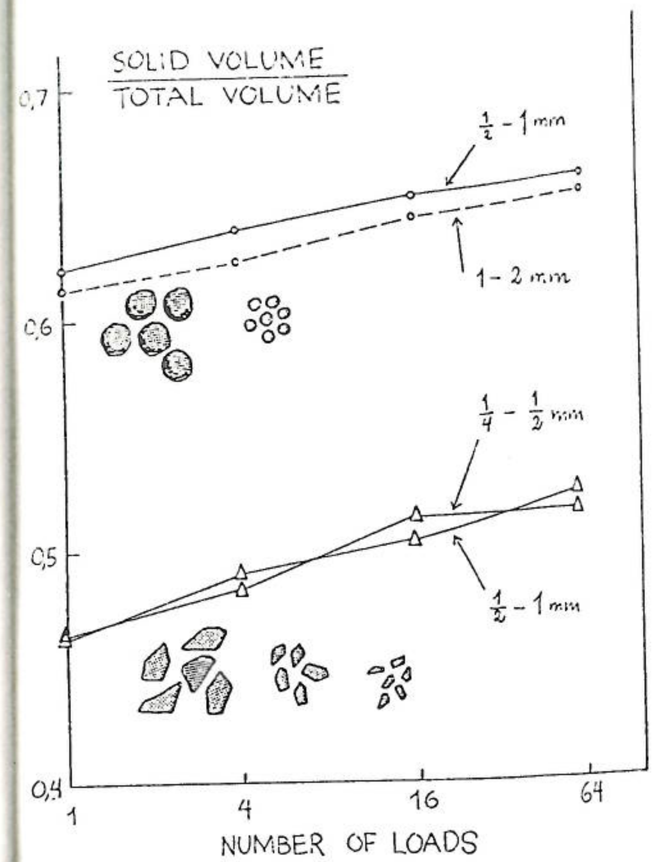


Fig. 3.1. Density of dry sand as function of number of strokes during compaction on a compaction table. At the top: rounded particles; at the bottom: angular particles.

The fresh paste consists of a high content of solid particles in a liquid medium. The basic principle is to arrange the particles in what is termed dense packing. The meaning of this is discussed in the following. In order to obtain the desired packing, the locking effect of attractive surface forces between adjacent particles must be largely overcome. »Overcome« is, however, a relative term. The effect of dispersing agents on the dispersion of cement + silica fume in water is essential for the achievement of the dense structure of the paste, i.e., low water requirement.

3.1 Principle of dense packing

Dense packing is the essential feature of DSP-materials. The new materials combine very densely packed cement particles, ultra-fine (silica) particles in the spaces between the cement particles and, normally, densely arranged fibres and/or aggregates.
The packing of particle systems in which surface forces are insignificant is independent of the absolute particle size, depending only on the shape of the particles, the relative size distribution and the mechanical placing of the particles, i.e. the kinematics. This means that regular packing of equal spheres results in the same volume fraction of solids (for example, 0.52 for cubic packing and 0.74 for hexagonal packing), irrespective of the absolute size of the spheres.

3.1.1 Effect of particle shape

The packing density depends on the particle shape: the more angular, oblong and rougher the particles, the lower will be the density. Examples of packing using sand with different particle shapes are shown in FIG 3.1.
In DSP-paste, the large particles (cement) normally have a cubic-angular shape, giving moderate packability, while the ultra-fine silica fume is spherical, resulting in ideal packing.
Densely packed elongated bodies, such as fibres, will normally be arranged in a much more open structure than compactly shaped particles unless special precautions are taken.

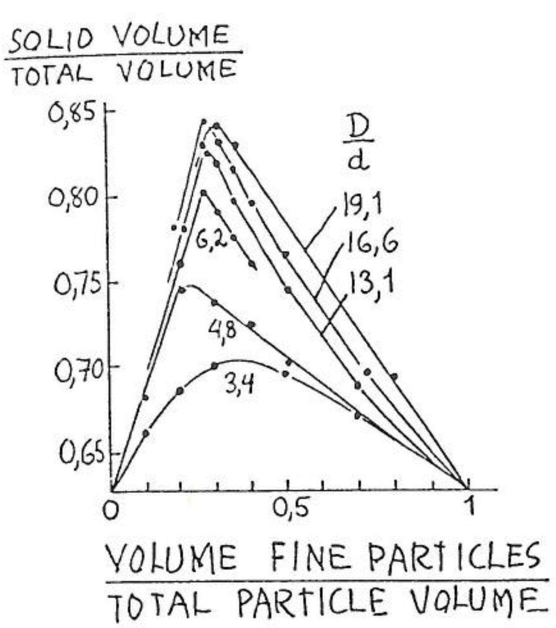


Fig. 3.2. Dependence of the packing density of spherical particles of two sizes on the volume content of fine particles in the mixture (% by volume) and the ratio of the diameters of the fractions. From bottom to top -curves for the following particle dimensions in the second fraction: d = 0.915; 0.66; 0.48; 0.19 and 0.165 mm (first fraction always D = 3.15 mm). [7]

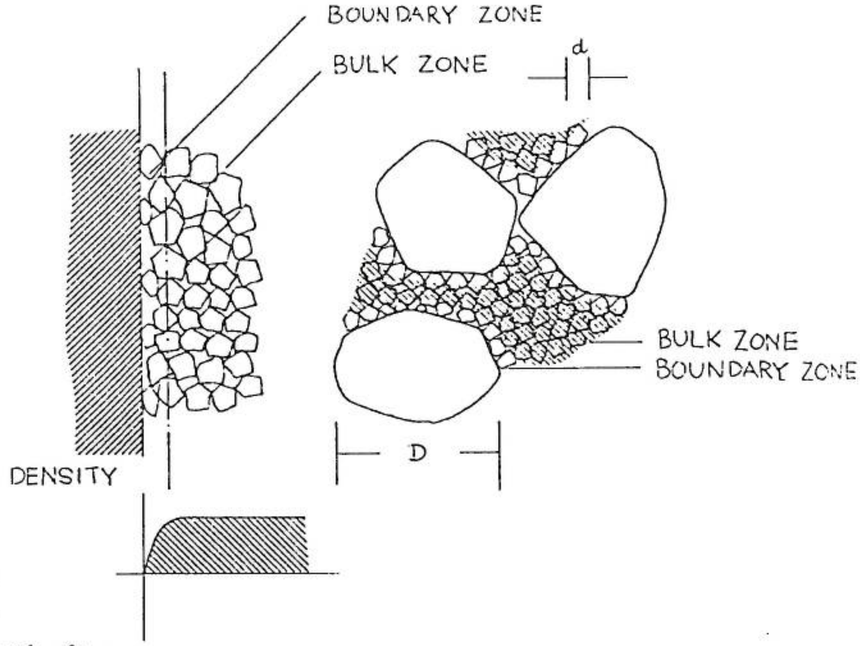


Fig. 3.3. Wall effect and barrier effect are expressions of the fact that particles are packed more loosely in the immediate vicinity of a surface than in the bulk and of the fact that there is not room for small particles in the narrow zones between big particles.

3.1.2 Effect of particle size distribution

The density is strongly influenced by the relative particle size distribution, that is, the ratio between the various particle sizes. Thus, Brown and Richards [6] report classic experiments with binary packings of spherical particles with various size ratios, where the volume fraction of the solid increased from about 0.63 for packing of each of the individual fractions to 0.70 for a mixture of large and small particles with a size ratio of only 3.4:1, and to 0.85 for a larger size ratio of 16:1. Similar results are shown in FIG. 3.2.

The densest packing in binary mixes is obtained with a high size ratio between large and small particles, typically in excess of 20:1.

When the size ratio is not very large, the packing density is reduced because of the wall and barrier effect (see FIG. 3.3).

Without this effect, 100% dense packing could be achieved in multi-component mixes by filling the spaces between the particles with successively finer particles.

This is not, however, possible in practice, where the ratio between the largest and the smallest particles is limited to about 10^4 for concrete with an aggregate size up to 10 mm and cement down to 1 μ. In such a system, a marked wall and barrier effect occurs if there are more than 3-4 discrete particle fractions.

There appears to be no theory from which we can determine a composite that will result in optimum packing. Instead, we must compromise between a few-component packing with little wall effect and barrier effect, on the one hand, and multi-component packings on the other. In each particular case, the optimum combination can be assessed by physical compaction tests. However, some general principles may usually be applied.

1. A densely packed particle fraction should be protected against dilution by ensuring a considerable gap in particle size (for both large and small sizes).
2. In the case of ultra-strong, cement-based materials, the dense packing of the strength-developing cement particles should be protected by using a relatively coarse sand for the bigger sizes and ultra-fine particles that are considerably finer than the finest fraction of the cement for small sizes.
3. Where other particles or fibres of cement fineness, e.g. 10-20 μ diameter glass fibres, are used in cement-based DSP, it is possible to compensate for the relatively high dilution of the cement fraction that takes place at the surface of these particles or fibres by adding a correspondingly higher proportion of ultra-fine particles.

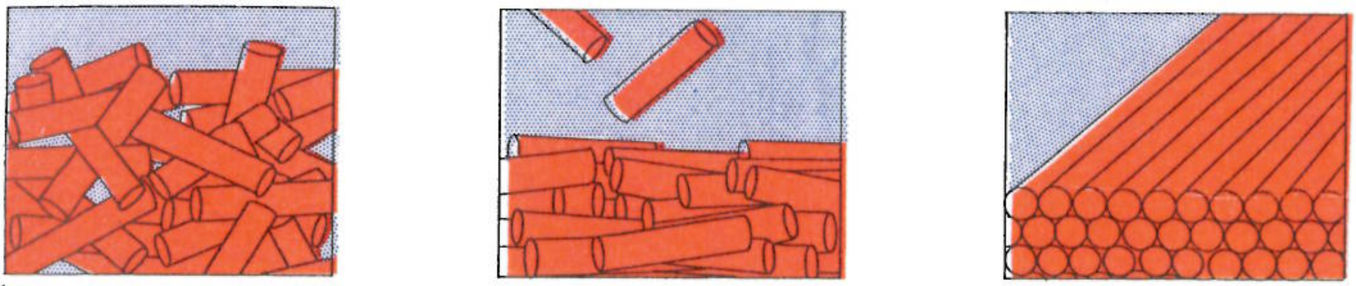


Fig. 3.4. Dense arrangement of fibres as obtained by
1) simple mixing and casting with the maximum fibre load limited by the mixing and shaping process only
2) sedimentation from a liquid with a low concentration of fibres in the absence of surface forces resulting in a rather dense packing because the fibres can turn freely into a horizontal position without interfering with settling neighbouring particles and
3) filament winding resulting in the most dense packing with parallel fibre arrangement.

3.1.3 Kinematics

The packing of bodies or particles where surface forces are eliminated is strongly dependent on the kinematics of the arrangement of the bodies. For example, fibres may be arranged in what is considered dense packing in the context of the present paper by 1) a simple mixing and casting process, 2) sedimentation, or 3) filament-winding as illustrated in FIG 3.4. The density or fibre concentration increases strongly from 1) via 2) to 3). Typical fibre concentrations obtained with these three methods are 5, 20 and 60 per cent volume, respectively.
The density of the packing of particles of compact shape is also strongly influenced by the mechanical compaction method. Simple pressure compaction will not normally result in very dense packing of particle systems in which the particles retain their geometrical identity (that is, are not crushed or heavily deformed).

Normally, denser packing can be obtained by shear deformation, repeated shear deformation, or balanced vibration, all with application of a small, normal pressure to ensure that the repeated deformation finally results in a denser structure. Some results are shown in FIG 3.1 and FIG 5.2.
For this reason, it is not possible to express dense packing in terms of one unique quantity. The »dense packing« referred to in this paper is to be understood as such dense packing as would be obtained in systems without locking surface forces.
It will thus be understood that the dense packing is the combined effect of the particle or body shape and the way the particles or bodies have been arranged, that is, the kinematics under conditions in which the particle or body concentration is insignificantly influenced by surface forces, as in DSP-materials.

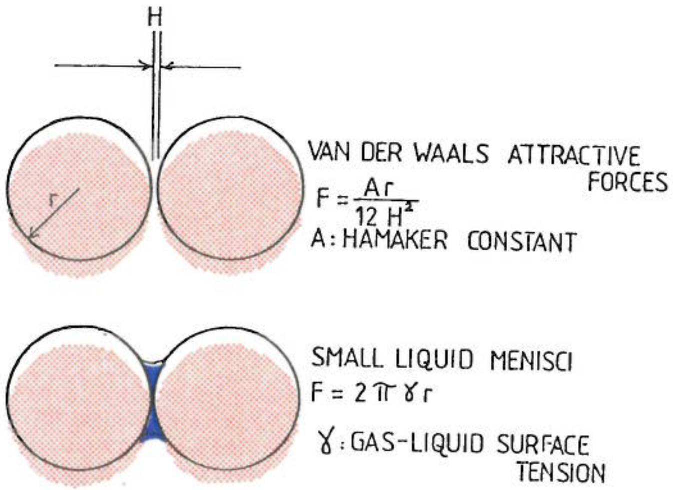


Fig. 3.5. Examples of attractive forces (F) between two spherical particles due to surface forces.

$F \propto \gamma d$

In Van der Waals attraction, $A/24\pi H^2$ is the surface energy required to release 1 unit area of new surface by removing plane parallel plates from the contact distance H to infinity. [8]

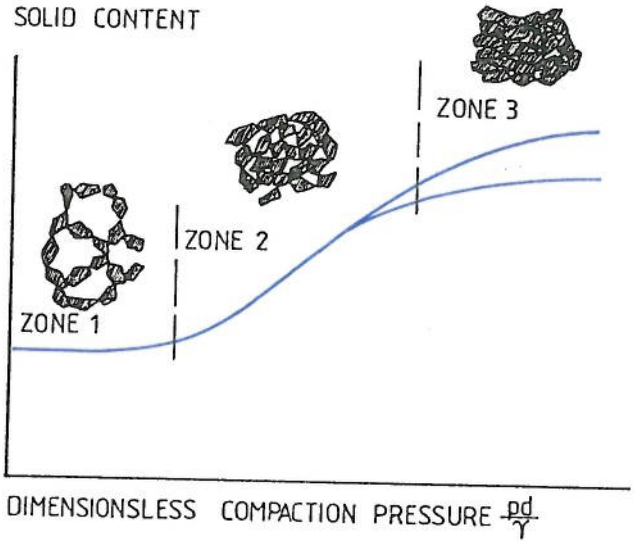


Fig. 3.6. Density of particle material as function of dimensionless compa tion load.
In zone 1, the surface forces which keep the material together agai external compression predominate. There is no yielding or compaction In zone 2, the external loads and internal coherence balance so that i ternal yielding towards a denser packing takes place with increased dime sionless pressure.
In zone 3, the external loads dominate over the surface forces between t particles. In this zone, the packing depends on the particle geometry and t type of compaction. [9]

3.2 Overcoming surface forces

For particles of compact, rounded shape, held together by surface forces, the forces required to separate two particles in point contact or to perform mutual sliding are proportional to the particle dimension (d) and the surface tension (γ) (see FIG 3.5)

$$F \propto \gamma d$$

On the assumption that separation and sliding resistance dominate over rolling resistance*, the yield stress for powder (which is proportional to the force acting on a particle, divided by the area of the particle) can be written

$$p \propto \gamma d^{-1}$$

or, in dimensionless form,

$$pd/\gamma = \text{constant}$$

where the constant is a function of the geometry c the particle system (relative particle size, shape an arrangement).

The quantity pd/γ is a measure of the extent to whicl external stresses (p) are able to overcome interna cohesion (γ/d) and has played an important role in th choice of strategy for the production of dense, strong cement-bound materials, including DSP. A grapl illustrating the principles of overcoming surface for ces in particle systems is shown in FIG 3.6.

Ultra-fine particles subjected to attractive surface for ces will usually be locked in a very open structure if th packing takes place under moderate external pres sure. In this case, we talk of a low, dimensionless com paction pressure pd/γ.

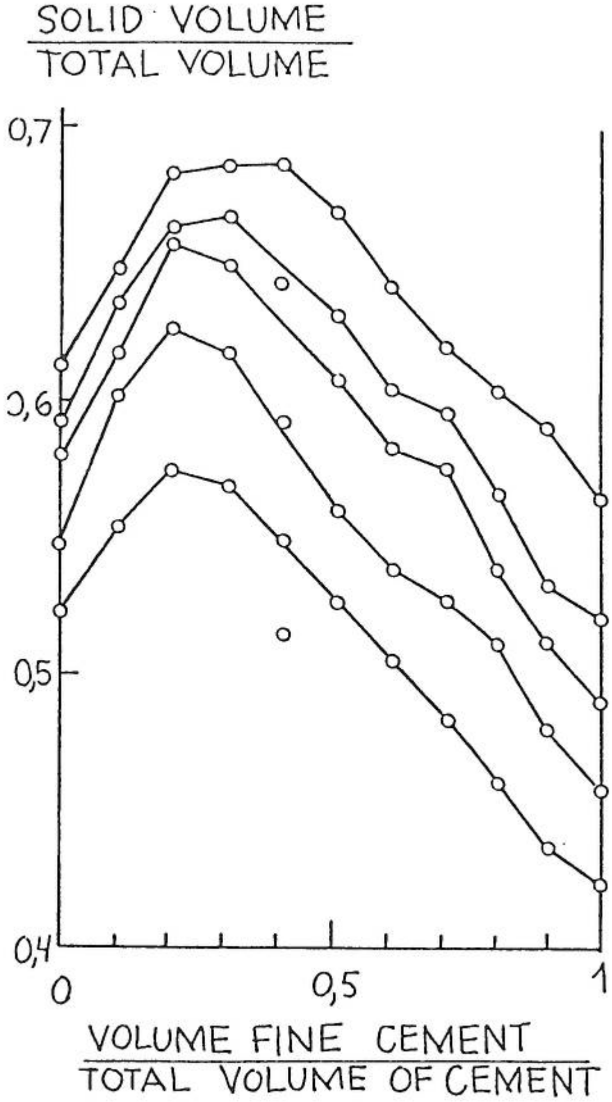


Fig. 3.7. Density of compacted, dry, special cement consisting of mixes of coarse cement (d ≥ 40 μ) and fine cement (d ≤ 2 μ) in relation to the mix ratio between coarse and fine cement. Compaction was performed by vibro-compaction using an electro-dynamic shaker with pressure ampitudes increasing from approximately 0.65 MPa (bottom curve) to approximately 13 MPa (top curve), with superimposed static pressure varied correspondingly from approximately 1.0 MPa to 14.5 MPa. Frequency: 100 Hz, vibration time: 1-2 minutes per loading stage.
The relative density of an ordinary, finely ground Portland cement compacted at 13 MPa was 0.65. [10]

As indicated in FIG 3.6, denser packing can be achieved by 1) heavier compaction (pressure p), 2) reduction of surface forces (γ), for example by means of surface-active agents, or 3) selection of larger particles (d). For very large values of pd/γ the locking effect of surface forces is practically overcome, cf. for example a pile of stones. Here, the particle packing is principally a question of particle geometry and the way in which the compaction is performed, i.e. by vibration. For small particles as in cement, however, surface forces can be the limiting factor. To overcome these forces, a high oscillating pressure (up to 13 MPa) was used initially as shown in FIG 2.1. and 3.7.
For DSP-materials, the locking effect of surface forces is almost completely eliminated by means of dispersing agents, thereby enabling ideal geometrical arrangements with packing of small particles between large particles to ensure a very dense structure despite the fact that the small particles packed between the cement particles are about 1/100 the size of normal cement particles (silica fume with an average diameter of 0.1 μ).

When other forces than contact forces are responsible for arranging fine particles - gravity, for example -principles similar to those discussed in terms of pd/γ may be utilized, but with different mathematical models. Thus, the dense arrangement of small fibres through sedimentation depends on whether the force of gravity (including buoyancy) acting on each individual fibre can overcome the surface forces tending to fix or lock the sedimenting fibre (such locking or fixation is usually fixation in an undesirable, not horizontal, position) so that the sedimenting fibre will obtain a desired, mainly horizontal position (see FIG 3.4).

In the case of rolling resistance, the mathematical expression has a slightly different form.

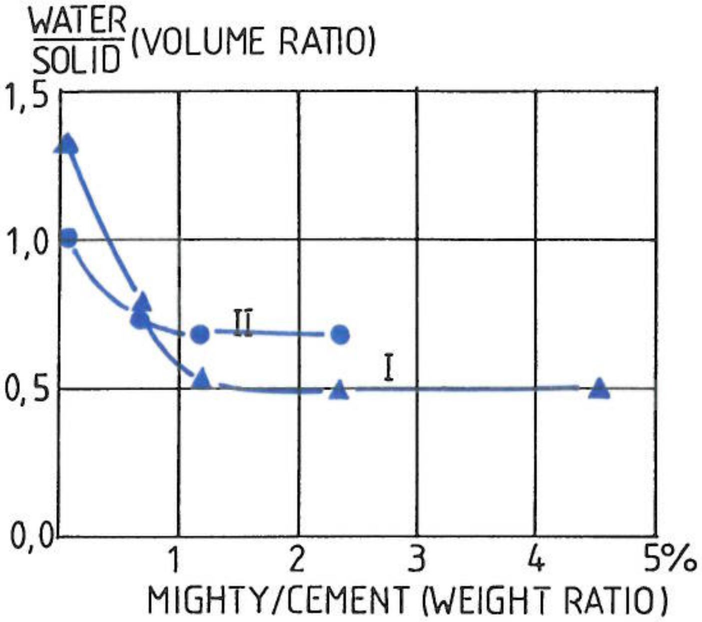


Fig. 3.8. Effect of amount of dispersing agent on the amount of water required to fluidize mortar with cement + silica (I) and cement only (II). The silica-cement-ratio in mix one was 0.71 by weight (1.0 by volume). The two mixes contained the same volume powder (cement + silica and cement respectively). The amount of dispersing agent is given as weight of dry powder in relation to weight of cement in mix II.

3.3 Function of dispersing agent in cement-based DSP

The purpose of a dispersing agent is to establish forces repulsing adjacent particles, thereby eliminating the blocking between the particles caused by mutual attraction.

It is believed that steric hindrance is required to disperse densely packed cement in water and that this is the basic function of typical concrete superplasticizers. However, it is thought that electrical repulsion also plays an important part.

Experience over many years indicates that pure electrical repulsion is insufficient to prevent flocculation of Portland cement in water. This is probably due to a high concentration of divalent and trivalent counterions (Ca^{++} and Al^{+++}), which, according to the Hardy-Schultz rule, compress the diffused double layer, and perhaps also due to the formation of direct chemical bonds. It seems likely that efficent dispersion of ordinary Portland cement in water is strongly dependent on dispersing agents engendering efficient steric hindrance.

The achievement of a good dispersion of ultra-fine silica, e.g. with an average size of 0.1 μ, in water, is basically simpler than the achievement of a similar dispersion of the much coarser Portland cement (which normally has an average particle size of 10 μ).

Efficient dispersion of colloidal silica in water can actually be achieved simply by pH control in the absence of salts [11]. When silica slurry is mixed with Portland cement, we have a different situation. Thus, a 1:1 mixture of silica fume (specific surface area 25000 m^2/kg) and tap water (by weight) and a 2:1 mixture of silica and 3% sodium tripolyphosphate* aqueous solution both result in slurries with moderate viscosity, which are easily mixed in low shear mixers or by hand. However, attempts to combine such silica/water systems with Portland cement have resulted in pronounced flocculation.

Thus, the addition of a small amount of a Portland cement/water slurry to a large batch of silica/water slurry results in a drastic stiffening, which makes further mixing impossible. This demonstrates that the matter dissolved from the cement flocculates the ultra-fine silica particles and that the specific dispersing agent does not prevent this flocculation. The precise mechanism of bond formation between the silica particles is not known, but the explanation is likely to be along the lines of reduced double layer repulsion and formation of various types of direct bonds.

Hence, the success of superplasticizers in ultra-fine particle/cement/water DSP-systems is not due to their ability to disperse the ultra-fine particles in water (indeed, other surfactants are even better for this purpose) but to the fact that they cause good dispersion of the silica in the specific Portland cement/water environment.

For cement-silica-based DSP-materials we normally use 1-4% dispersing agent (calculated as weight of solid in relation to weight of cement). In most of our experiments, the concrete superplasticizers used are sodium salts of condensed naphthalene sulphonic acid/formaldehyde condensates.

The relationship between the quantity of superplasticizers and the water requirement for a DSP-mortar is shown in FIG 3.8. It has been found that there is a saturation point for superplasticizers, beyond which practically no effect is observed. The saturation quantity is strongly dependent on the type of cement and increases with decreasing water/cement + silica ratio.

*Sodium tripolyphosphate is a common dispersing agent.

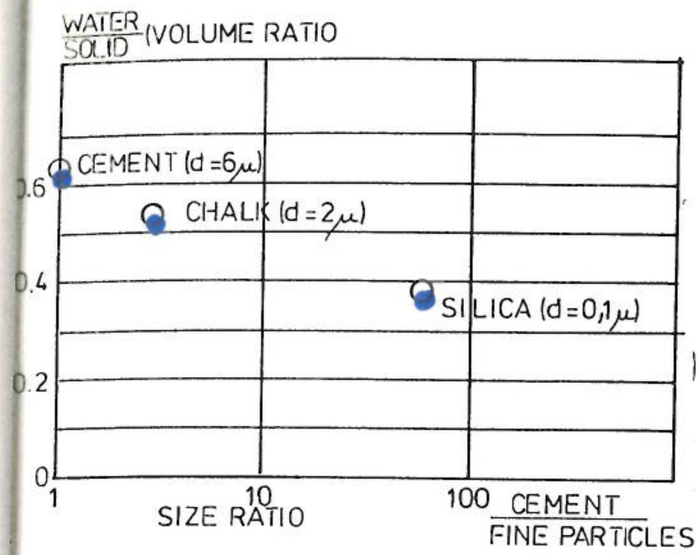


Fig. 3.9. Water requirement to fluidize a mortar by replacing part of the cement with fine particles (25% by volume), using a large amount of superplasticizer.

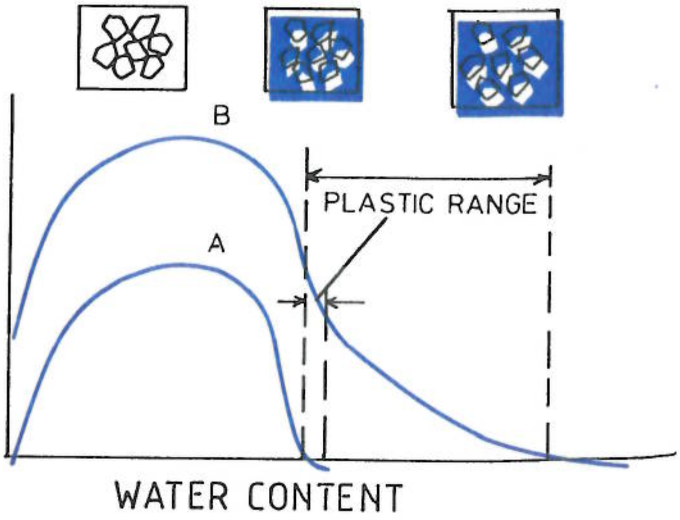


Fig. 3.10. Cohesion as a function of water content in granular materials with and without directly acting surface forces (b and a). The particle arrangement is kept uniform as the water content is increased up to saturation. Any further increase in water content results in a more open particle structure.

3.4 Water requirement

The effect on the water requirement of replacing part of the cement in a superplasticized mortar by fine particles is shown in FIG 3.9. This figure and FIG 3.8 illustrate that this reduces the water requirement considerably when the material is well dispersed. When this is not the case, the water requirement increases.

The amount of water required to achieve an easily castable, plastic to fluid DSP-material is thus considerably lower than that used in ordinary superplasticized concrete or mortar (typically between 0.12 and 0.18 by weight).

The low water requirement is due to the very dense packing of cement with the addition of 10-50% by volume ultra-fine particles in the spaces, leaving only a small volume to be occupied by liquid, since for particle systems in which the effect of locking surface forces is insignificant, the water requirement is basically a question of saturation. This will be dealt with in more detail in the following.

Cohesion of a powder is discussed below, under reference to FIG 3.10.

Materials without effect of locking surface forces in the saturated state (pd/γ *large)*

In the completely dry materials there is no internal cohesion. When water is added, liquid menisci are established, which hold the material together. As saturation is gradually approached, these menisci are removed, and the internal resistance (cohesion) falls abruptly towards zero. In this case, the water requirement corresponds approximately to the compacted particle system being just saturated.

The transition from stiff, plastic consistency to completely liquid consistency takes place in a very narrow range, for example from a water/powder ratio of 0.13 to 0.15 for well dispersed cement-silica DSP-paste.

Materials with significant effect of locking surface forces (pd/γ *small)*

We will now consider particle systems in which contact forces act directly between the particles - for example, in cement paste without dispersing agents or in clay.

In the dry state, the particles are held together by directly acting surface forces with air in the spaces between the particles. When water is added, liquid menisci are established, increasing the internal resistance. As saturation is gradually approached, the menisci disappear and the internal resistance decreases to a level determined by the directly acting surface forces.

A further increase in the water content is now accompanied by a more open particle structure, which becomes gradually weaker as the water content increases, until - at a critical water content - the material liquifies. The greater the effect of directly acting surface forces, the higher will be the water requirement and the less sharp the transition from plastic to fluid behaviour.*

According to the model pd/γ, in ordinary mortar or concrete without plasticizers, the locking effect of surface forces, the quantity of water required to fluidize the paste and the plastic range all increase with increasing fineness of the cement used. Thus, the addition of silica fume with a specific surface area of 25000 m^2/kg to a cement paste without dispersing agents would considerably increase the water requirement and the plastic range (see FIG 3.9)

**The amount of water required to change the consistency from plastic to fluid is commonly termed »the plastic range«.*

In cement-water suspensions with *efficiently acting dispersing agents* eliminating the effect of direct attraction between neighbouring particles, the situation is quite different. Irrespective of the particle size, the water requirement is reduced to that required to saturate a particle system in which the pore volume to be filled is only a question of the geometry of the particle system (relative particle size, particle shape and internal arrangement). Thus, in experiments by Brunauer and co-workers [13], superplasticized, very fine cement (specific surface 600-900 m^2/kg) had a water requirement of only 0.2-0.3 (by weight in relation to the cement). The water requirement was only one-half to one-third that of ordinary cement paste without dispersing agents, even though the Brunauer-cement had a far bigger specific surface area than ordinary cement.

By adding 20-40% ultra-fine, spherical silica particles (specific surface 25000 m^2/kg) in the spaces between densely packed cement in an aqueous dispersion, we reduce the pore volume and hence the water requirement (typically to 0.13-0.18 by weight of cement + silica). In the efficiently dispersed cement system or cement/ultra-fine particle system, the plastic range is only about 2% (by weight of the cement + silica).

Much finer colloidal silica (specific surface 200,000-380,000 m^2/kg), mixed with cement and dispersing agents, results in a considerably higher water requirement and a bigger plastic range, illustrating less efficient elimination of directly acting, locking surface forces.

In accordance with the model pd/γ, extremely dense packing of materials with such fine particles requires correspondingly greater mechanical stress (p) during shaping.

In the literature on concrete it is often stated that fine particle systems require more water due to the bigger surface area to be covered with water. The statement does not lead to false conclusions for ordinary, fresh concrete without surface-active agents, where a finer cement actually does require more water, although not due to the size of the area to be covered with water, but to the fact that the locking surface forces have a greater effect on a fine particle system than on a coarse system. It is also in accordance with experience to say that the water requirement for concrete decreases with increasing size of the largest aggregate. The reason, however, is not that the larger aggregates have a smaller surface to be covered with water, but simply that, owing to the wall and barrier effect, a particle system with a larger range of particle sizes packs to higher density than one with a smaller range, leaving less space for the water.

In connection with superplasticized particle systems, the statement that the water requirement increases with increasing specific surface area is meaningless and misleading, since here, the water requirement is only a question of filling spaces. The statement would, in fact, have militated against the development of DSP-materials because it would mistakenly have warned against the use of ultra-fine particles as a means of achieving a high degree of packing (low water requirement).

The geometrical aspect of the water requirement for DSP-materials is demonstrated by premixing a cement-rich mortar with a large amount of a concrete superplasticizer and a small amount of water (w/c = 0.18). Even after a very long mixing time, the mix has the appearance of a dry, slightly wetted powder because there is too little water to saturate the material. We then add dry silica fume with a specific surface area of 25,000 m^2/kg in an amount corresponding to 25% of the cement by weight. (The bulk volume of the fine, loosely packed powder is the same as the volume of the entire batch of mortar after mixing).

After a few minutes' mixing, the mix changes to a wet, plastic to viscous mass, well suited for casting under slight vibration.

What we have done is simply to arrange the ultra-fine particles in the spaces between the densely packed cement particles, thereby reducing the space to be filled with water.

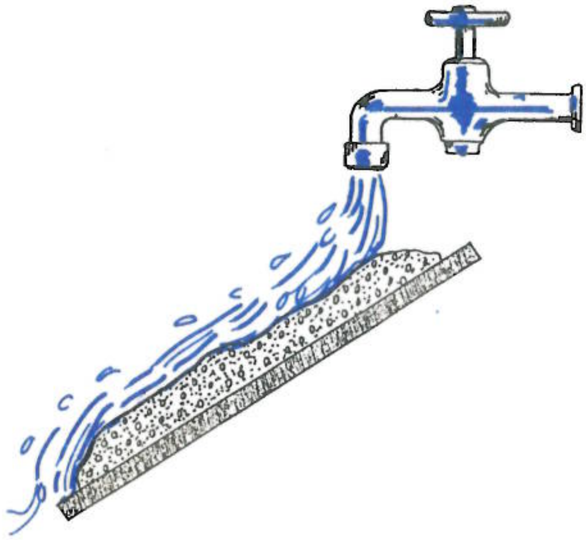


Fig. 3.11. demonstrates the internal coherence of fresh DSP-mortar when placed under tap water (rate of flow about 4 litres per minute). In this demonstration, the mortar was usually kept under the flowing water for periods of 2 - 30 minutes without any visible washing-out of the components.

3.5 Water retention

One of the major advantages of DSP-materials over ordinary cement materials is that the former are shaped with a very dense structure from a plastic to fluid mass, substantially without water being moved or squeezed out during the shaping process. This is due mainly to the fact that the ultra-fine particles efficiently reduce the rate of internal liquid flow.

The squeezing out of liquid from saturated particle systems depends on compressing the particle skeleton - and on the flow of liquid through the channels between the particles.

For materials with identical particle geometry, the time required for squeezing liquid out is (according to Therzaghi [14]) given by

$$\frac{\Delta\theta}{\Delta\theta_{t=\infty}} = \text{function of } \frac{td^2E}{H^2\eta}$$

where $\Delta\theta$ is the change in porosity, t the time, d the particle size, η the viscosity of the fluid, E the modulus of elasticity of the particle skeleton, and H a characteristic dimension of the body in the direction of drainage.

By using ultra-fine particles, for example 60 times finer than the cement particles, we increase the consolidation time by about 60^2 in relation to a pure cement system. This means that when the characteristic drainage time for cement paste is x seconds, the corresponding drainage time for DSP-paste is x hours.

In practice, that means that there is no water separation on account of gravity-caused consolidation (bleeding) and that pressure-moulding in the plastic state is not, as in the case of ordinary cement materials, impeded by locking friction forces caused by water being squeezed out of the heavily loaded zones*.

In addition, the strongly reduced internal water transportation in fresh DSP-materials helps to give the material great internal coherence, which manifests itself, for example, in very high resistance to bleeding in fresh condition, making the material particularly suitable for underwater casting. The great internal coherence is demonstrated in FIG 3.11.

3.6 Structure formation

Basically, we still lack a detailed picture of the chemical structure formation. However, experience in connection with setting and hardening shows that:

1. the setting time is considerably delayed due to the large amount of dispersing agent. The setting time at 20° is usually between 6 and 18 hours;
2. after setting has commenced, the reaction is rather fast;
3. DSP concrete and mortar have been cured in the temperature range 0-216° C with good results judging from the strength of the hardened material;
4. in the first 24 hours after mixing, the DSP-paste usually contracts considerably - up to twice as much as ordinary cement paste;
5. owing to its extremely low water content, the freshly cast material is more sensitive to evaporation than is ordinary cement paste.

*For high-pressure extrusion of cement products, so-called thickeners are normally used, which delay liquid extrusion by making the vater viscous.

Structure and properties of hardened material

4 Structure and properties of hardened material

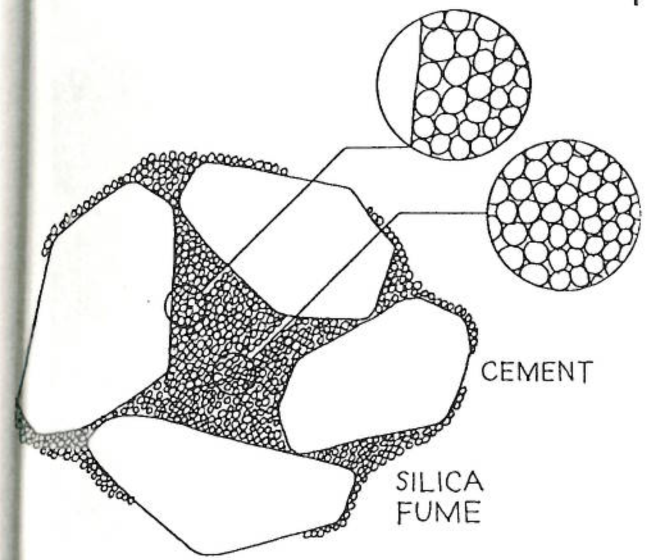


Fig. 4.1. Questions regarding structure formation within the ultra-fine particle structure in cement-based DSP. Is there a higher concentration of hydration products near the surface of the cement as in the bulk (b)?. Do the fine particles contain non-movable water in the meniscus after movable water has been used for chemical reactions? Does precipitation on the fine particles take place mainly in the contact zone between the ultra-fine particles? To what degree do the fine particles participate in the chemical reactions?

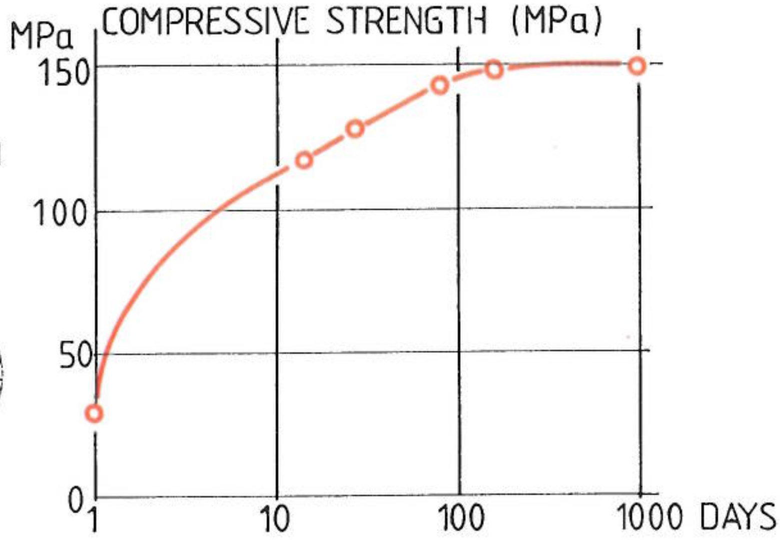


Fig. 4.2. Compressive strength of DSP-concrete cured at 20°C in water, measured on cylinders 10 cm in diameter and 20 cm in height.
Compositon in kg per cubic metre:

Silica fume	*133*
Portland Cement	*400*
Quartz sand 1/4-1 mm	*141*
Quartz sand 1-4 mm	*566*
Crushed granite 8-16 mm	*1153*
»Mighty« (powder)	*13.5*
Water	*100*

Consistency of fresh concrete: soft
Compaction: vibration for 10-20 sec. at 50 Hz.

The micro-structure of hardened DSP-paste based on Portland cement and silica fume seems to be far more dense than ordinary cement paste. This impression is based on experience regarding drying, pressure saturation, ion transport, freezing, impressions from scanning electron microscopy and expectations from our knowledge of the dense micro-structure of the fresh paste.

However, we lack a detailed picture of the micro-structure, and there are still a lot of questions to be answered, see FIG 4.1.

From a large number of mechanical tests on composites, a few tests on paste and predictions based on the structure, we can conclude that the pure paste is very strong, rigid and brittle. However, systematic investigations of the mechanical behaviour of the pure paste have not yet been made.

With the limitations imposed by the lack of precise knowledge of the micro-structure and of the properties of the paste, the following description concentrates on the composite materials and, especially, on a discussion of ways of developing such materials with desired properties, such as volume stability and ductility.

4.1 Mechanical properties

4.1.1 Compressive strength

Easily flowing concrete made from ordinary aggregates and about 400 kg cement and 80 kg silica fume per cubic metre and a large quantity of superplasticizer (typically 1-4% of the weight of the cement and silica calculated as dry powder) is normally made with only 80-90 litres of water - corresponding to a water/cement + fine powder ratio of 0.16-0.18, with a strength of 110-160 MPa.

Results from the first two batches of DSP-concrete demonstrate the strength development over a period of three years, see FIG 4.2.

In concrete with the new binder and with ordinary aggregates, the sand and stone are relatively weak components, as illustrated by the fact that rupture almost always passes through the sand and stone particles (see FIG 4.3).

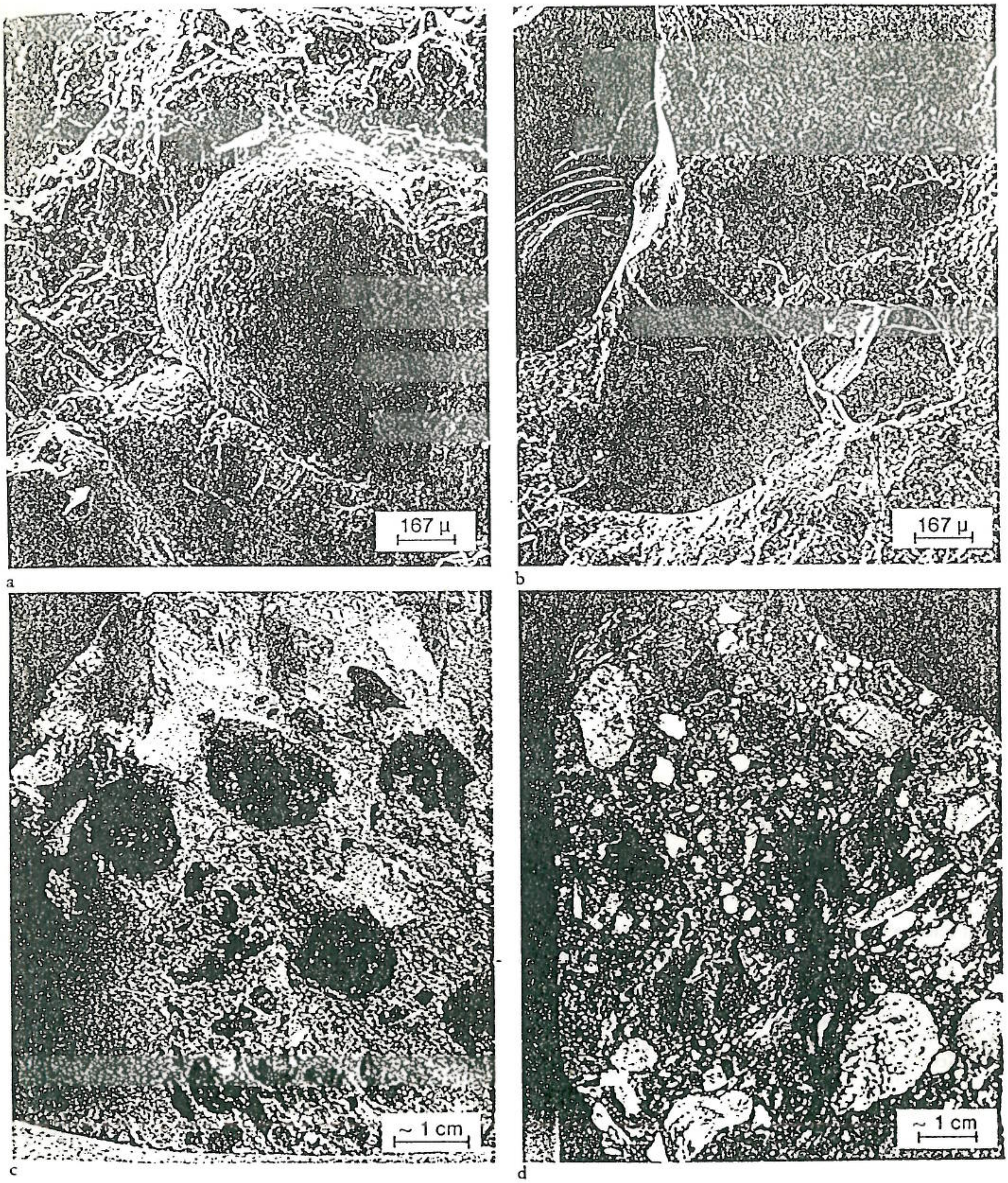


Fig. 4.3. Rupture faces in mortar and concrete made with ordinary cement paste (a and c) and with the new binder (b and d). The sand in the mortar (a and b) consists of rounded quartz particles. The stone material in the concrete (c and d) is marine aggregate. With the new binder, the rupture passes mainly through the aggregate particles.

Type of concrete or mortar (Max. size aggregate)	Density kg/m³	Compressive strength MPa	Sound velocity m /sec	Dynamic modulus of elasticity MPa	Stress-density ratio m²/sec²
16 mm granite*	2500	124,6	5200	68000	49840
16 mm diabas	2666	168,1	4890	65000	63050
10 mm calcined bauxite	2878	217,5	6150	109000	75573
4 mm calcined bauxite	2857	268,3	6153	108000	93910

Table 4.1.
Mechanical properties of soft cast DSP-mortar and concrete, results on 10 cm diameter 20 cm high cylinders water-cured 4 days at 60–80°C.
** (water-cured 28 days at 20°C strength development up to 3 years shown in FIG 4.2).*

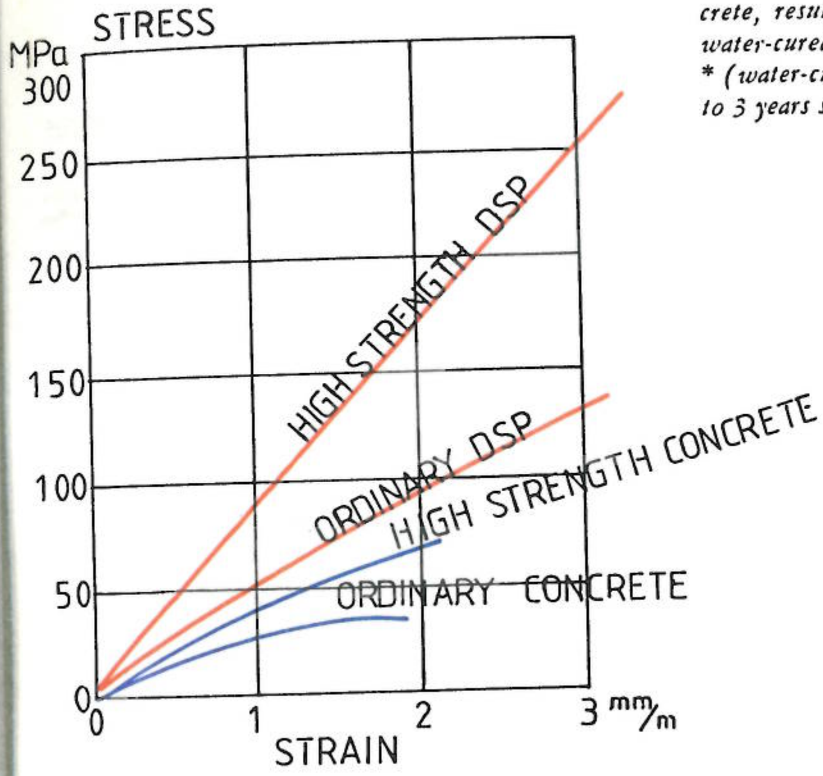
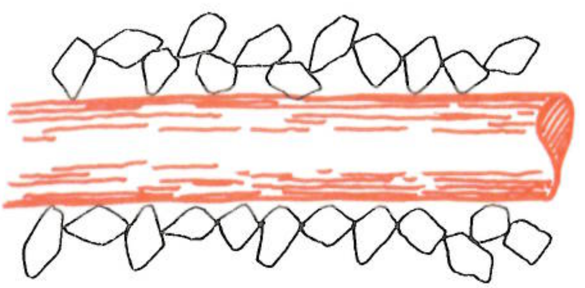


Fig. 4.4. Stress-strain diagrams for ordinary concrete and DSP-materials. The two upper curves show a mortar with up to 4 mm calcined bauxite, and a concrete with natural aggregates respectively. The figures in the brackets indicate the compressive strength in MPa. (The strength development for the DSP-concrete is shown on Fig. 4.2.)

No significant improvement is normally achieved by using exceptionally strong aggregates in ordinary concrete, since, in this case, the strength depends almost exclusively on the strength of the cement paste, which is usually low in relation to that of the aggregates.
However, in concrete with the new binder, characterized as a composite with aggregates that are weak compared with the matrix, an increase in the strength of the aggregates will have a pronounced effect on the strength of the concrete [15].
The use of stronger aggregates together with the new, dense and strong binder has resulted in considerably increased strength, for example, a cylinder strength of 268.3 MPa has been achieved in a mortar made of sand consisting of up to 4 mm calcined bauxite (test specimens, 10 cm diameter x 20 cm cylinders, cured for 4 days at 80° C - average of 14 tests). Some data are shown in *table* 4.1, from which it will be seen that the new high-strength materials are 3-5 times stronger than normal concrete.
The very high-strength bauxite-based materials are typically used for high abrasion resistance (for example as linings in pipes for the transportation of coal, fly ash, cement, bauxite, etc.), for safes and for tools for pressure moulding.

4.1.2 Modulus of elasticity

Without reinforcement, the new materials are distinctly brittle, with a straight stress-strain curve right up to failure, as illustrated in FIG 4.4. The modulus of elasticity (the slope of the curve at low load) is in the range of 50,000-90,000 MPa, in other words 1.5 to 2 times that of ordinary quality concrete (see also *table* 4.1).



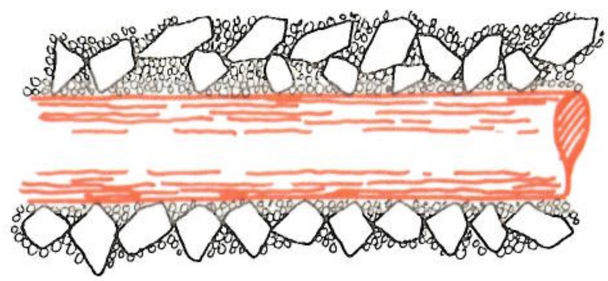


Fig. 4.5. Fine fibres embedded in cement paste (left) and in the new binder (right).
The mechanical fixation of the fine fibres is greatly increased by incorporating the fine particles in the spaces between the densely packed cement because the dimensions of roughness and wave configuration on the reinforcement that are necessary for »mechanical locking« of the reinforcement in the matrix are thereby strongly reduced

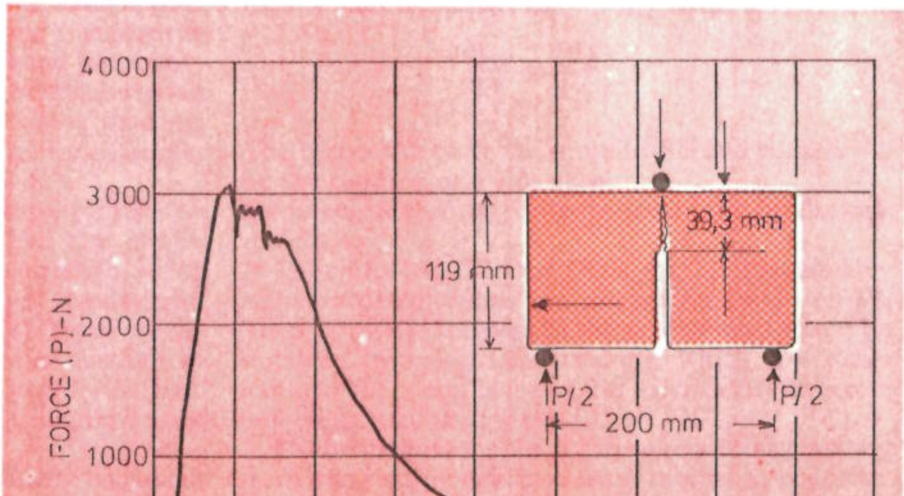


Fig. 4.6. Energy consumption at crack opening in notched specimen. The specimen was cut from a 21 x 600 mm silica-cement-paste plate made by extrusion with about 4% by vol. 6 mm special polypropylene fibres. The energy consumption is determined on the basis of the shown relationship between the force and the displacement of the force.
The area below the curve is a measure of the work required to open a crack (cross-sectional dimensions 39.3 x 21.3 mm). This corresponds to an energy per unit area of about 9 kJ/m². The arrow indicates the direction of extrusion. The rate of loading is 0.5 mm/minute.

4.1.3 Anchorage of reinforcement (fibres)

The new binder results in improved anchorage of reinforcement. Pull-out tests on very smooth 6 mm steel bars embedded 60 mm in mortar based on the new binder resulted in a pull-out force of about 9 kN, compared with about 2 kN for ordinary mortar.
The very dense micro-structure of the binder makes it particularly suitable for mechanical anchorage of thin fibres, which are not normally fixed very firmly in cement paste, see FIG 4.5. This has been demonstrated by tests on a large number of laboratory-made and factory-made specimens, consisting of the new binder reinforced with very short, thin, plastic fibres (about 4% volume, 6 mm long, special polypropylene fibres [12]). The fibres are able to give the strong brittle matrix a high degree of ductility (see FIG 4.6).

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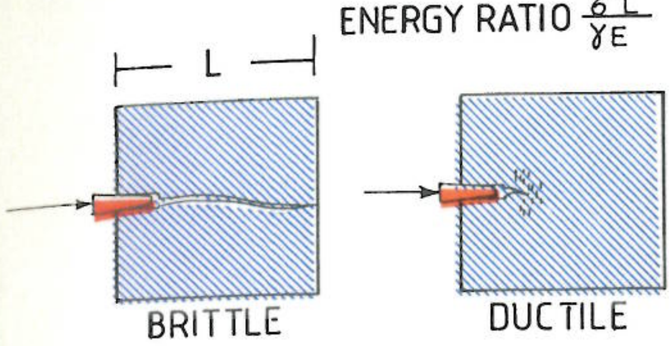


Fig. 4.7. Brittle and ductile behaviour of strain-loaded members. Characteristic size L, modulus of rupture σ, modulus of elasticity E, and energy to create a unit area of new surface γ. When the ratio of stored elastic energy before crack opening ($\sigma^2 L^3/E$) to energy necessary to create a continuous crack (γL^2) is large, the rupture is brittle, typically resulting in the crack running right through the body. When the ratio is small,only local crack opening and yielding occur.

4.1.4 Fracture mechanics (brittle and ductile behaviour)

The new binder is very strong, but also very brittle, like glass, and is thus, in itself, unsuitable as a structural material. The paste must be combined with other materials - sand, stone, fibre, reinforcing steel, etc. - to induce structural ductility. This situation is familiar from normal cement-based materials, from which we know that big bodies of unreinforced cement paste are distinctly brittle and crack easily during drying or heating, whereas, when combined with sand, stone, reinforcement, etc., the material forms a less brittle structure that is well suited for structural purposes.

It is a well known fact that distinctly brittle materials rupture very suddenly under local strain loading, often resulting in total collapse, as, for example, when a pane of glass breaks, cf. FIG 4.7a.

Such behaviour is obviously unacceptable for structural members (unless it can be ensured that strains never - even locally - exceed the ultimate strain, which would normally be a totally unrealistic requirement for cement-based products). It must therefore be ensured that the bodies are given greater ductility, so that strains that locally exceed the rupture or yield strain only result in local, permanent structural change (failure or yielding), cf. FIG 4.7b.

The transition between brittle and ductile behaviour can be evaluated on the basis of the ratio between stored elastic energy immediately prior to the commencement of rupture and the energy required for forming new surface when a continuous crack occurs. When the stored elastic energy is greater than the surface energy,sufficient energy is available to form the continuous crack, whereas the crack propagation would not be total if the released elastic energy were lower than the surface energy.

The transition between brittle and ductile behaviour can be profitably discussed in the light of dimensional considerations. For geometrically similar objects of characteristic length L, the stored elastic energy immediately prior to commencement of cracking is proportional to the elastic energy per unit of volume, multiplied by the volume of the object:

$$W_E \propto \frac{\sigma^2 L^3}{E}$$

where σ is the maximum stress immediately prior to cracking and E is the modulus of elasticity.

The energy required for forming a continuous crack is proportional to a characteristic surface energy (γ), multiplied by the area of the surface formed.

$$W_S \propto \gamma L^2$$

from which we obtain the energy ratio

$$\frac{W_E}{W_S} \propto \frac{\sigma^2 L}{E\gamma}$$

The bigger the ratio, the more brittle and sudden will be the rupture, and vice versa.

Let us consider some consequences of this for the new materials:

1. Unreinforced DSP-materials exhibit considerably more brittle behaviour than normal cement materials. Thus, an 8-fold increase in the energy ratio would be obtained by using DSP-concrete, which is 4 times stronger than, and twice as stiff as, ordinary concrete (assuming unaltered γ and L).

2. The brittleness of objects can be reduced by moving from paste to mortar, and from mortar to concrete, since the incorporation of sand and stone increases the energy to create a new surface (γ)* and themodulus of elasticity (E), while often (although not always) reducing the ultimate stress (σ).

3. The only way to give DSP-materials ductility is to incorporate high-energy-absorbing reinforcement (bars, wires, fibres etc.).

4. The brittleness of objects increases with their size L. Thus, large structures require more energy-absorbing reinforcement than small members.

**The effect of sand and stone on the fracture energy in normal cement-based materials has been studied by Matz Moder [16] inter al. The capacity of aggregates for reducing brittleness is probably less pronounced in DSP-materials unless very strong aggregates are used.*

4.1.5 Creep and shrinkage

The low water content and dense structure of DSP-paste give reason for supposing that creep will be smaller than in ordinary cement paste. The same arguments can be advanced with regard to drying shrinkage, but that illuminates only one aspect of the material's behaviour during drying.

In drying shrinkage, the contractive forces are much greater than in normal cement paste due to the very dense and very fine micro-structure, which, all else being equal, should result in greater shrinkage. It is not possible a priori to predict the combined effect of the more rigid structure and the increase in contractive forces.*

The creep and shrinkage can be considerably reduced by incorporating a large amount of sand and stone - as is well known from ordinary concrete - since most of the deformation occurs within the paste.

Due to the improved flow properties of the fresh DSP-paste it is generally possible to introduce a higher volume of sand and stone than in ordinary concrete, thereby increasing the volumetric stability still further. Investigations of creep and shrinkage are in progress.

4.2 Durability

The new binder is, in general, far more durable than ordinary cement paste, primarily because of its extremely dense structure.

4.2.1 Frost resistance

In a very severe freezing test on concrete** it took nine months to destroy the DSP-specimens, whereas reference specimens (including some made with high-quality superplasticized concrete with a w/c ratio of 0.25) were all destroyed in less than two weeks. In these tests, destruction was defined as a 50% reduction of the sound velocity.

In tests on the durability of factory-made edge beams for a highway bridge, it was found that members made of DSP-material completely survived a severe freeze-thaw test which destroys traditional, high-quality concrete [17]. The main results are shown in *table* 4.2.

**In this paper, shrinkage refers to volume change of hydrated material due to drying. The volume change during the early hydration is treated in 3.6.*

***The testing involved the following daily exposures:*
(1) in 7.5% NaCl-solution at 20°C for 2 hours
(2) drying in air at 105°C for 4 hours
(3) in 7.5% NaCl-solution at 20°C for 2 hours
(4) in air at -20°C for 16 hours
Over weekends the specimens were stored in the NaCl-solution.
Test specimens: cylinders, diameter 10 cm height 20 cm.
The mix composition of the DSP-concrete is shown in FIG 4.2.

Concrete Type	Cement kg/m³	Silica kg/m³	Air content %	Water/powder ratio	Compressive strength MPa	Length change mm/m		
						Number of cycles		
						96	241	337
Ordinary Quality concrete	330	–	6-8	0.38	65	cracked after 44 cycles		
Fiber concrete	450 + (180 fly ash)	–		0.45	25	3.3	5.8	6.5
DSP concrete	500	100		0.19	130	0.0	0.0	0.2
DSP concrete	220	110		0.30	100	0.0	0.0	0.2

Table 4.2
Results of freezing test on concrete for edge beams using the following method:
Test specimens (30x30x70 mm prisms) were sawed out. Two 50 mm taps spaced at an interval of 50 mm were glued on to each of the four long sides of the prisms. After storage in water for one week, prisms were stored alternately for 10 minutes in water at 20° C and 20 minutes in a saturated solution of NaCl at -15°C.
The distance between the measuring points was recorded at about every 50 cycles.

In another experiment, the amount of freezable water in DSP-paste was investigated in a temperature range 0 to -50° C by low temperature micro-calorimetry (Bager and Sellevold [18]):
10 mm thick specimens were made with a water/cement + silica ratio of 0.13 in a laboratory extruder. The paste contained about 4% polypropylene fibres by volume [12]. The specimens were
1) cured in water at 20° C for about 3 weeks
2) cured in water at 20° C for about 6 months, and
3) cured in water at 20° C for about 8 months, dried in air at 50° C and resaturated (after evacuation) under a pressure of 150 atm.

In all the experiments, the amount of freezable water was about 5 milligrams per gram specimen, and the freezing occurred in the range of -35 to -45° C.
As the water content (determined by drying at 90° C in air at 2.5 torr) was about 80 milligram per gram, the results indicate that only about 6% of the water in the narrow pores froze when cooled down to -50° C.
Bager and Sellevold state that 1) the amount of freezable water is substantially lower than in normal cement paste, 2) freezing occurs at a much lower temperature, and 3) the material is insensitive to a drying-resaturation process, which substantially increases the amount of ice formed in the high-temperature range (above -20° C) in ordinary cement paste.
It seems that the frost resistance of DSP-materials in general is of a completely different order of magnitude than that of ordinary air-entrained concrete.

4.2.2 Protection of steel and glass

The high density and low water content promise good protection of reinforcement, However, this assumption naturally requires verification, and investigations are in progress to determine the degree of protection afforded to both steel and glass reinforcement.
A major project on the ability of the material to protect steel against corrosion has started at the Danish Corrosion Centre. Preliminary electro-chemical investigations indicate greatly increased resistance to corrosion. For example, it is mentioned in [19] that the electrical resistance is about 10^6 Ω cm, which is 2 to 3 orders of magnitude greater than that of ordinary cement mortar and concrete.

4.2.3 Chemical resistance

The new binder is attacked by the same chemicals as ordinary cement paste. Thus, like this, it is not acid-resistant. However, on account of the great density of its structure, the binder is affected more slowly.
A major study of the suitability of the material for encapsulating radioactive waste has started at the Risø National Laboratory. In this connection, it is particularly the dense structure of the materials, combined with the simple casting technique, that is of interest.

5 Applications

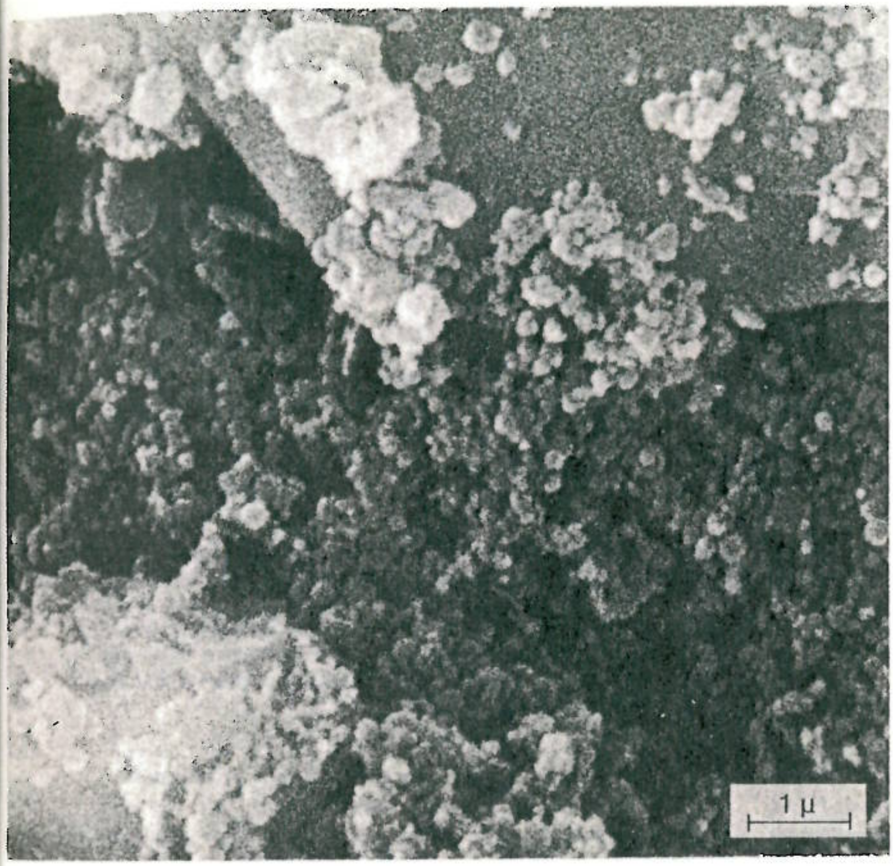


Fig. 5.1. Cement and silica particles. The cement particles (top right and bottom left) have a particle size of about 10 μ. The silica particles have a size of about 0.1 μ. SEM-photo of dry powder.

Principles for using the new binder materials are given in the following. It is important to develop composite materials that combine the excellent properties of the binder with other desirable properties that this does not possess.

5.1 Materials

The matrix of the new materials is composed of the following types of components:

1. a powder with a particle size of 0.5-100 μ, e.g. ordinary Portland cement with a specific surface area of 300-500 m^2/kg, which, in aqueous surroundings is transformed into a solid structure due to hydraulic properties;
2. an ultra-fine, comparatively less reactive, inorganic powder with a particle size that is 10-100 times smaller than that of the cement, i.e. silica fume composed of spherical particles with a specific surface area of about 25000 m^2/kg;
3. a surface-active agent that ensures good dispersion of the above-mentioned powders in water without impeding the chemical structure formation during hydration of the cement, for example an agent of the sulphonated naphthalene formaldehyde condensate type;
4. water.

A SEM-photo of the dry cement and silica fume is shown in FIG 5.1.

5.2 Mix composition

A wide variety of mix compositions are used for various purposes: soft-cast concrete and mortar; extruded, fibre-reinforced cement paste; fluid injection grout; concrete for gunnite; etc. Examples are given elsewhere in this paper.

A typical mix composition consists of: 1) a paste with 10-50% silica fume (in relation to the weight of the cement), 1-4% concrete superplasticizer (referring to dry powder) and a water/cement + silica-ratio from 0.12 to 0.30; and 2) as much sand, stone and other bodies as possible.

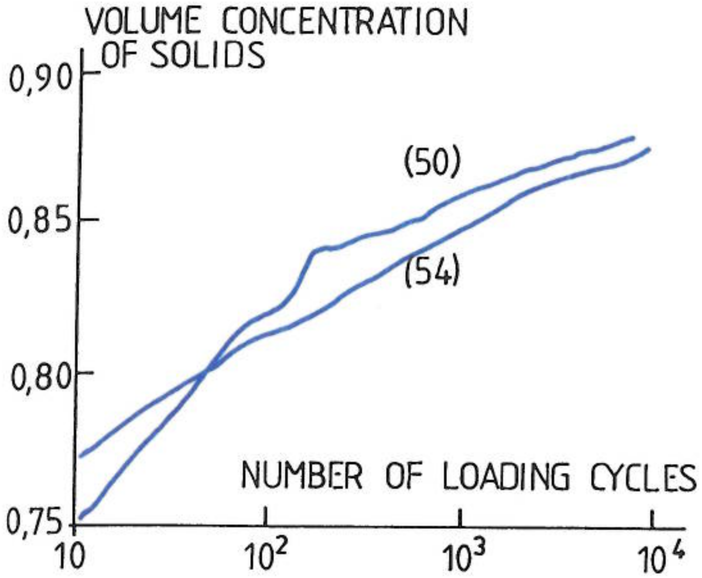


Fig. 5.2. Change in density of ordinary concrete during vibro-compaction. The concrete contained stone up to 8 mm and had cement contents of 300 and 375 kg/m³, respectively, and water-cement ratios of 0.35 and 0.31 (relating to specimens 50 and 54, respectively).
The pressure amplitude in the vibro-compaction was approximately 2 MPa, and the frequency was 50 Hz. [20]

5.3 Vibratory compaction

Despite the good flow properties of fresh DSP-materials, it is advisable to use mechanical compaction where practically feasible, in order to enable incorporation of a high concentration of sand and stone to ensure volumetrically stable, less brittle concrete or mortar.
Vibration is suitable for this purpose due to the ability of granular materials to pack increasingly densely under repeated loading. The effect of the number of loadings on the packing of particle systems is illustrated in FIG 3.1 and 5.2. However, compacting forces must act at the same time if the oscillating loads from the vibration are to have a packing effect instead of a loosening effect; for this reason, use of moderate static pressure can be recommended. In order not to lock the particle system, the static pressure must not be too high in relation to the oscillating pressure.
In effectively dispersed materials like fresh DSP-materials, where the internal cohesion is overcome, there is normally no need for very heavy vibration compaction. Owing to the high solid content of the paste, DSP-concrete will often have a relatively high viscosity, resulting in considerable damping of mechanical oscillations. This results in a considerably smaller action range for the vibrators and an extended vibrating time.

5.4 Underwater casting

On account of great internal coherence, DSP-materials are particularly suitable for underwater casting by simply dumping the material into the water.
DSP-materials seem to open the way for various new developments within the field of underwater concreting:
1. the production of high-quality, reinforced, underwater DSP-concrete by underwater injection of pre-packed aggregate and reinforcement with DSP-mortar or paste;
2. underwater repairs and injection;
3. precision casting under water - for example, for reproducing archaeological or geological structures - where the low viscosity of the material in the fresh state and high strength in the hardened state can be used to obtain precise, mechanically strong castings that reproduce even the very smallest details.

5.5 Injection

DSP-materials are highly suitable for injecting in ducts for post-stressed concrete on account of their extremely good flow properties and inner coherence in the liquid state (no bleeding), combined with great density and strength in the hardened state.
Cable ducts are traditionally injected with cement paste without sand and stone in order to ensure good flow and filling of narrow zones that would be blocked by big particles. However, because of the wish for increased volumetric stability and less brittleness of the grout, a mortar or concrete would be preferred for filling purposes instead of paste if a suitable material could be produced.

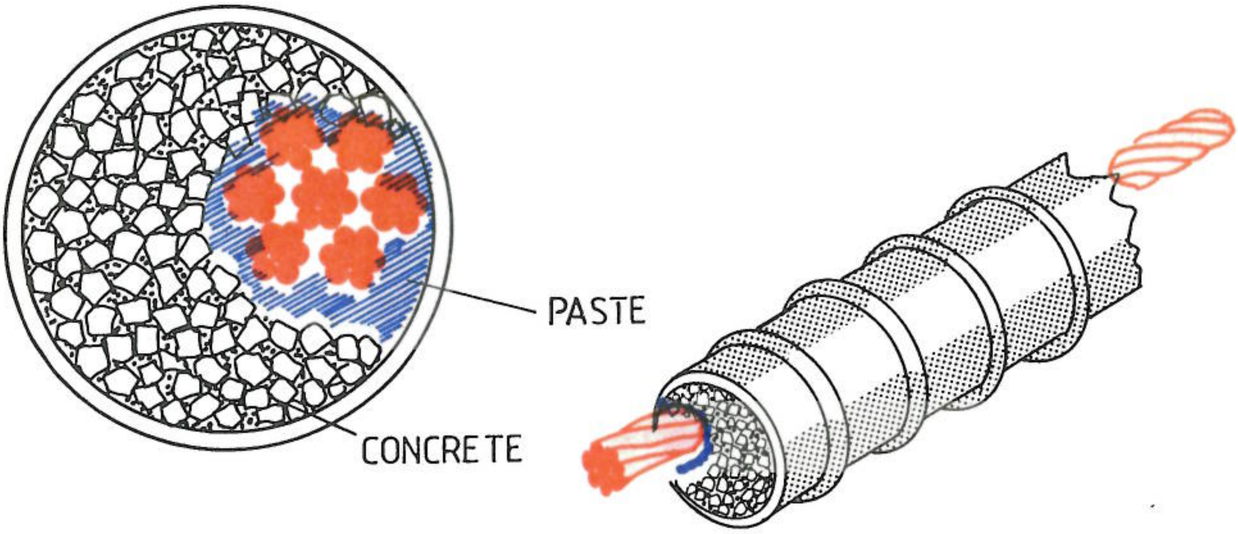


Fig. 5.3. Two-stage injection of space between duct and cable. First fine DSP-paste is injected. This is followed by a DSP-mortar or concrete, which displaces the paste in the bulk zone. (sketch showing principles).

Owing to the good flow properties of the new material and its great internal coherence, it is possible to inject a mass with a very high concentration of big particles provided that the cross section of the duct is big in relation to the maximum particle size in order to avoid particle-blocking. This important factor is not, in itself, sufficient to ensure the desired high-quality filling, because the presence of the big particles effectively prevents the material from filling narrow zones. In order to counteract this effect, a method based on multi-phase injection is proposed (see FIG 5.3). According to this method, fine-particle material - for example DSP-paste - is injected first, filling out the whole of the cross section, including the narrow, inaccessible areas. A coarser DSP-material (mortar or concrete) is then injected; this does not have the same ability to penetrate narrow zones, but is, on the other hand, able to displace the fine-particle injection mass from the big, accessible zones, which now, as desired, become filled with coarse-particle-based DSP instead.

5.6 Reinforced materials

With the greatly increased strength of the binder matrix and the vastly improved fixation of fibres and bars in the matrix, the possibility arises of producing new classes of reinforced and fibre-reinforced, cement-based articles and materials:

1. materials with very high tensile strengths obtained by incorporating high-quality, fine fibres or whiskers (fibres or whiskers of high tensile strength and high modulus of elasticity, for example glass fibres, carbon fibres, asbestos, Al_2O_3 whiskers) in a medium to high volume concentration in the binder matrix.
2. Materials with high tensile strength and comparatively large strain capacity obtained by incorporating high-quality, relatively fine fibres with a high tensile strength and relatively low modulus of elasticity in a medium to high volume concentration in the binder matrix (for example, high-strength polypropylene fibres or Kevlar fibres).
3. High-performance, prestressed, reinforced articles, the quality being primarily obtained by incorporating a much bigger volume of high-quality steel bars or wires than ordinarily used (the volume of reinforcement that can be utilized being directly proportional to the compressive strength of the matrix). The volume of prestressing steel is as low as 1-2% in ordinary prestressed concrete. The volume of the steel is limited by the compressive strength of the concrete. An increase in the compressive strength by a factor of 4 could, for example, be fully utilized in prestressing members to secure a 4 times higher bending capacity. Such members would require a not unrealistically high volume of prestressing steel (4-8%). It would also be possible to use the improved matrix material in prestressed elements of much smaller cross section than in traditional prestressed concretes, with a corresponding use of fine prestressing reinforcement (thin wires).

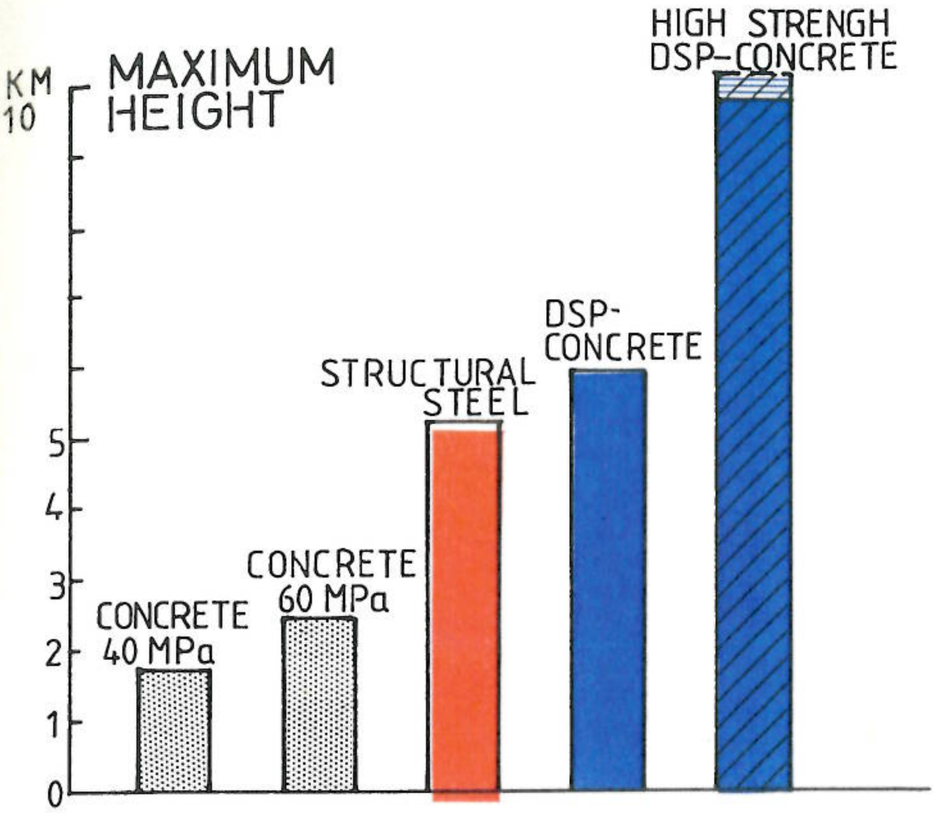


Fig. 5.4. Maximum height of vertical prisms determined by the stresses at the bottom being equal to the compressive strength (for ordinary concrete and DSP-concrete) or the yield value (for structural steel).
The highest value of compressive strength of a single DSP cylinder was 282.7 MPa, which, with a specific weight of 2861 kg/m³, corresponds to a stress-density ratio of 98812 m²/sec² and a maximum height of 10076 m.

Table 5.1
Strength and density of materials. The strength value for structural steel refers to the yield value.

4. Elements of reinforced, non-prestressed concrete, where the improved quality of the matrix material is primarily utilized by incorporating steel bars or wires of higher tensile strength than in ordinary steel-reinforced concrete. The greatly improved fixation obtained in the binder matrix opens up the possibility of a beneficial utilization of the very high strength wires and bars as non-prestressed reinforcement. Due to large strains (when fully utilizing the high steel quality) and the corresponding cracks that occur in the concrete (as in normal reinforced concrete), it is particularly advisable to use the above-mentioned technique in thin members in combination with fine reinforcement in order to secure a crack pattern with several finely distributed, thin cracks.
The reinforcing possibilities mentioned can, of course, be combined in many ways, for example by making a thin cover of fibre-reinforced material on a large steel reinforced member, or by using high-quality steel wires as secondary reinforcement (mainly placed perpendicular to the main reinforcement) in large prestressed members.

5.7 Large structures

With the development of DSP-materials, we have the means of building far bigger structures - bridges, towers and similar -than has hitherto been possible. This is due not only to the high strength of DSP-materials, but also to the fact that the material is relatively light (compared, for example, with steel), for which reason it is particularly suitable for carrying its own weight.
In very large structures, the predominant force is either the force of gravity F_g (which is proportional to the volume) or the wind load F_w (which is proportional to the exposed area of the structure):

$$F_g \propto \rho g L^3$$

$$F_w \propto p L^2$$

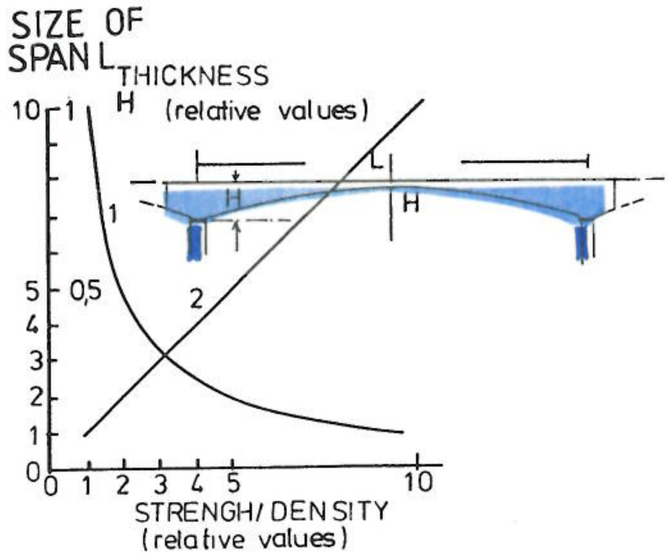
The resisting forces stabilizing the structure are typically proportional to a cross section area multiplied by acharacteristic yield or rupture stress (σ)

$$F_r \propto \sigma L^2$$

The ratios between the forces tending to cross the structure and the resisting forces are

$$(1)\quad \frac{F_g}{F_r} \propto \frac{\rho g L}{\sigma} \quad \text{(when gravity predominates)}$$

$$(2)\quad \frac{F_w}{F_r} \propto \frac{p}{\sigma} \quad \text{(when wind load predominates)}$$



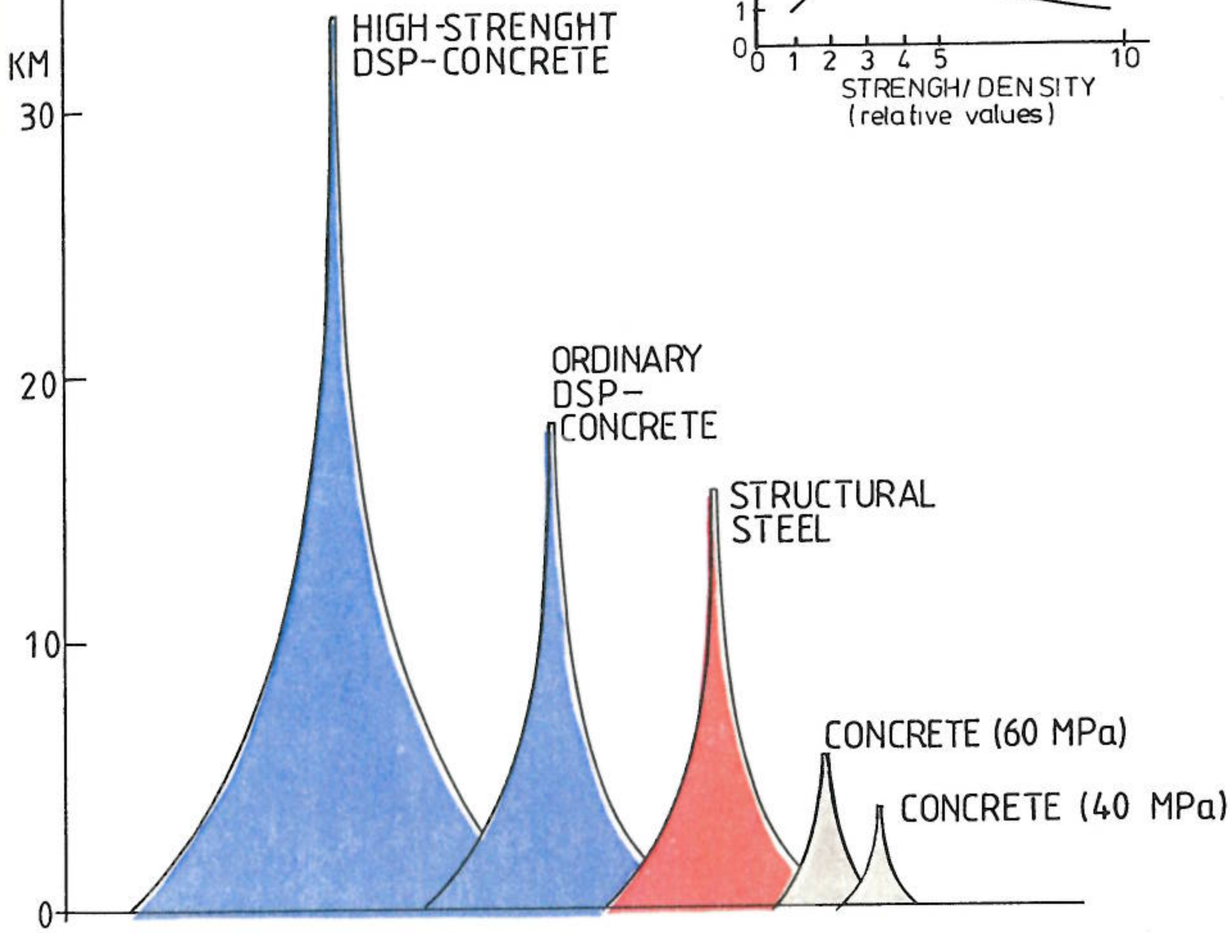


Fig. 5.5. Maximum size of large towers designed to carry only their own weight.
Assumptions: material properties as indicated in table 5.1., factor of safety 2.5.
Diameter at top of tower 200 m
Slope at bottom 1:1.
The shape of the towers is given by

$L = L_c \ln (d_c/d)$

where L is the height, L_c is a critical length, and d and d_c are the diameter at the height L and at the bottom.

($L_c = 2\sigma/\rho gf$, where the factor of safety $f = 2.5$).

5.7.1 Gravity-loaded structures

From (1) it will be seen that the maximum size (L) of structures in which gravity predominates is proportional to the stress-density ratio: σ/ρ Some values of stress-density ratios are shown in *table* 5.1.
It will be seen that the stress-density ratio for DSP-materials is normally 3-6 times that for concrete and somewhat higher than that for high-quality structural steel.
This factor is further illustrated in FIGs 5.4, 5.5 and 5.6.

With reference to FIG 5.6, it should be noted that reduction of thickness to about 1/4 and 1/6 of that of ordinary concrete by replacing ordinary concrete by cement-based DSP-concrete with ordinary aggregates and strong aggregates, respectively, hardly alters the quantity of reinforcement required at all, since the reduced weight almost exactly compensates for the reduced moment arm (we do not have full compensation due to the fact that DSP-concretes are 10-20% heavier than ordinary concrete).

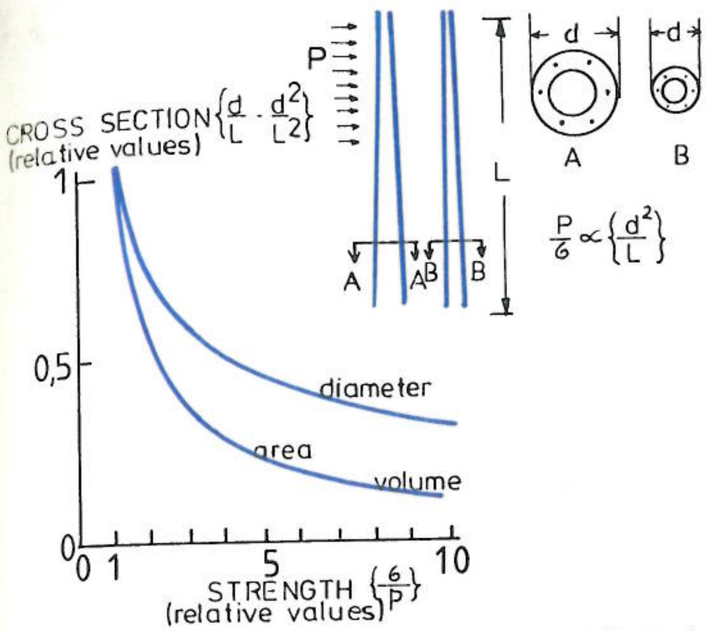
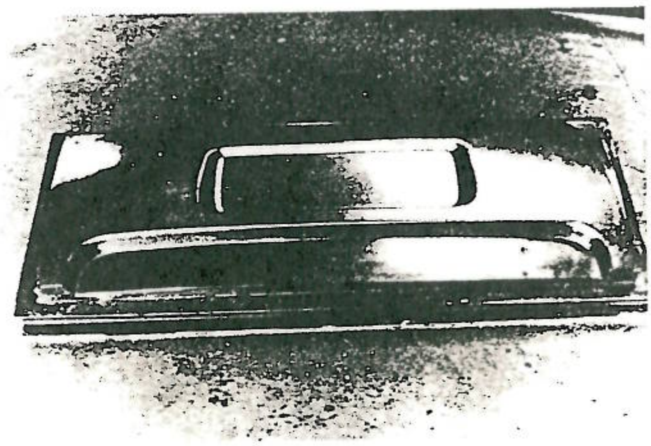


Fig. 5.7. Large bending members designed to withstand wind load only. The curves indicate minimum cross-sectional dimensions, section areas and volumes of large bending members with similar cross sections as functions of the bending strength, assuming constant length and wind load. The illustration on the right shows two structures where B is made of 4 times stronger material than A, resulting in a 50% reduction of the transverse dimensions and a reduction of the cross sectional area and volume to one quarter. The quantity of reinforcement remains unchanged.

Fig. 5.8. a) Chassis component made of 9 mm steel plate pressed in DSP-mortar tools.



b) Top part of tool for pressing 1300 x 800 mm chassis component. The top and bottom parts of the pressure tool are made of DSP-mortar cast against original component [21].

5.7.2 Wind-loaded structures

It will be seen from (2) that the stress (σ) in wind-loaded structures of identical geometry depends only on the wind load (p), independent of the absolute size L. High-strength materials can thus be used to achieve more slender masts, towers,etc.

The relationship between the strength and the slenderness of wind-loaded structures is shown in FIG 5.7. From this it will be seen, for example, that an increase of the strength by a factor of 4, obtained by using cement-based DSP-concrete, can be utilized to halve the cross section of a mast or chimney and to reduce the volume to 1/4, while the quantity of reinforcement remains unchanged. The latter factor is due to the fact that the reduction of the moment arm to one half is compensated by a similar reduction in the load on account of the smaller mast cross section.

5.8 Press tools

DSP-materials are extremely suitable for press tools where exact reproduction of a given shape is desired. This is due to the ability of the material to reproduce a surface geometry down to the very »smallest detail«*, while retaining high mechanical strength, combined with the fact that the press tools can be made by a simple casting method at room temperature.

Use of the material for pressure-casting polymers is one of many interesting suggestions. The material can also be used for pressure-shaping steel plates, for example for car chassis, for which machined stee tools are normally used (see FIG 5.8). Such pressur tools are typically made of fibre-reinforced DSP mortar with sand of calcined bauxite.

It must be presumed, as a first approximation, that the size of the smallest detai correctly copied by a particle material is proportional to the size of the smalle significant particle fraction, which, for DSP-materials, is about 0.1 μ.

6 Concluding remarks

I believe that the use of geometric and kinematic principles for arranging micron and sub-micron size particles - made possible by superplasticizers - is the key to the development of a wide variety of new, high-quality materials.

For cement-based materials, improved equipment for mixing, shaping, etc. would probably produce significant improvements in quality. Experience from the paint industry and other industries that use sub-micron size particles would probably be highly useful. Research along the lines of surface and colloid science and investigations into the microstructure of the hardened materials are strongly recommended.

Terminology and notation

DSP refers to "Densified Systems containing homogeneously arranged ultra-fine Particles", as explained on page 5

The silica fume consist of spherical particles of amorphous SiO_2 (90-96 %) with an average diameter of about 0.1 μ (BET-surface 25000 m^2/kg) and density 2200 kg/m^3.

The calcined bauxite consist of about 85 % Al_2O_3. The density of sand and stone is about 3300 and 3100 kg/m^3 respectively.

Compressive strength refers, in the present context, to cylinders of height 20 cm and diameter 10 cm.

Dispersion, in the present context, is to be understood as dividing agglomarates of particles into smaller units.

Dispersing agents are additives which assist the dispersion.

Superplastisizer is a type of dispersing agents used in Portland cement/water systems.

Electrical repulsion is explained in the classical D.L.V.O. theory [8], which states that electrical charges exist on the surfaces of particles and that these charges give rise to electrical double layer in a ionizing medium. These in turn give rise to repulsive forces when two particles approach each other.

Steric hindrance prevents particles from coming together due to the presence of adsorbed layers of another compound on their surface.

Dimensionless compaction pressure $\frac{pd}{\gamma}$ is the ratio between the external load on a powder mass and the internal resistance, as explained on page 12

E	modulus elasticity	[Pa]
g	acceleration of gravity	[ms^{-2}]
p	external stress, wind load	[Pa]
γ	surface energy, surface tension	[Nm^{-1}]
η	viscosity	[$N \cdot s\ m^{-2}$]
ϱ	density	[$kg\ m^{-3}$]
σ	strength, stress	[Pa]
$\propto$	varies directly as	i.e. proportional to

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