PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Development and Application of High-Density Cement-Based Materials [and Discussion]

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Development and application of high-density cement-based materials

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The properties of cement-based binders change dramatically when ultrafine particles are homogeneously placed in the spaces between densely packed cement grains. The increased density and the refinement of the pore structure of such binders result in considerable increases in properties such as compressive strength, impermeability and adherence to fibres and aggregates. It has been shown that such cement-based binders may be processed by simple techniques, and that the resulting materials may replace metals, ceramics and plastics.

Introduction

In the cement and concrete industry, the research and development organizations have often felt a challenge to increase the strength of cement-based materials. The maximum compressive strength of concrete is used as a direct measure of the development possibilities. In a few cases only, the tensile strength has been used as a similar measure although increase in tensile strength offers a wider scope for development.

As the strength increases with decreasing porosity and with smaller pore sizes (Powers *et al.* 1963, Birchall *et al.* 1981) the main principle in the development work towards increased strength has been to reduce the total porosity of the cement paste and to optimize the pore size distribution by various techniques. These techniques have included:

(i) mechanical treatments of the cement paste such as vibrational compaction (Bache *et al.* 1968), high pressure pressing (Roy *et al.* 1973; Lawrence 1969) and high shear mixing (Birchall *et al.* 1980);

(ii) the use of effective cement dispersing compounds, which reduce the water content necessary to obtain a 'workable' consistency of the cement paste (Hattori 1978);

(iii) filling up the pores with solid materials, such as sulphur (Malhotra 1975), and resin (Idorn *et al.* 1974);

(iv) the use of cements with special particle size distributions, such as very fine-grained cement (Brunauer 1972), and gap-graded cement (Birchall *et al.* 1980).

The present paper describes results from the industrial development of high-strength cement-based materials in which several of these principles are combined.

During the development work of these materials, extremely high compressive strengths were achieved, but it was also found that other properties were changed considerably, and realized that a new class of materials might be produced (Bache 1981). For the sake of brevity the new materials are termed D.S.P. materials referring to 'densified systems containing homogeneously arranged ultrafine particles'.

Properties of D.S.P. materials

D.S.P. binders may be produced from Portland cement, microsilica and superplasticizers. Superplasticizers are very effective dispersing agents often used in the concrete industry to reduce the water required to achieve a workable concrete. Microsilica is a by-product from the silicon and ferrosilicon industries. It has been used for some years to improve the properties of concrete (Hjorth 1982). Microsilica particles are spherical in shape and have an average diameter of about 0.1 μm. This size is about two orders of magnitude smaller than the cement grains, which indicates that microsilica may act as a microfiller in between the cement grains. Since microsilica is almost pure amorphous silica, it reacts chemically with the ions in the alkaline pore solution of the cement paste, forming reaction products which resemble the hydration products, found in ordinary, hardened cement paste. The D.S.P. binders consist of densely packed cement and these ultrafine microsilica particles homogeneously arranged in the space between the cement grains.

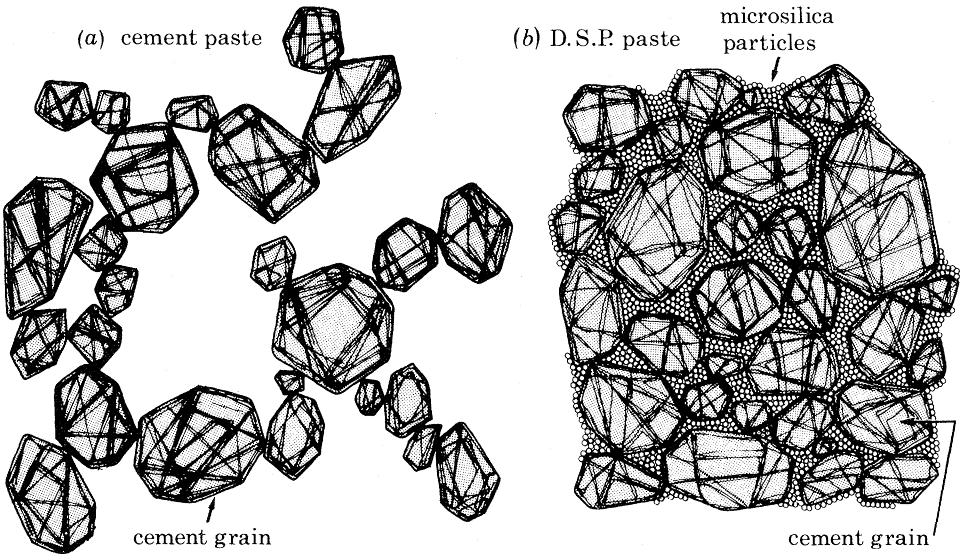

Figure 1. (*a*) Flocculated particles in ordinary cement paste. (*b*) Densely packed cement grains and microsilica particles in D.S.P. paste.

Production of the new materials is made possible by the superplasticizers, which change the flocculent, fine particle systems of cement and microsilica to systems that can be densely packed in a low stress field. Figure 1 (*a*) illustrates the difficulty of achieving dense packing of the cement particles, which is because the suspension of ground cement clinker plus gypsum in water is strongly flocculated (Diamond 1980). The cement grains adhere to each other, and the surface forces between the particles tend to prevent them from sliding relative to each other during mixing and casting. Figure 1 (*b*) illustrates, in contrast, the effective dispersing action of superplasticizers in deflocculating the system and enabling dense packing of the cement grains, and the microsilica particles in the voids between the cement grains.

The D.S.P. materials constitute a range of composite materials, comprising D.S.P. binders and additional solid particles such as aggregates and fibres. The properties of these materials can be varied considerably according to the composition and to the processing technique. The water to powder ratio (i.e. water to cement plus microsilica ratio) of these materials is generally within the range 0.12–0.22.

Such materials can be designed to have consistencies ranging from 'flowing' to 'plastic'. They can, therefore, be easily processed by simple techniques such as casting. More sophisticated processing techniques such as extrusion and rolling may also be applied, owing to the high internal cohesion, which is characteristic of D.S.P. materials. The strength properties are illustrated in figure 2, which shows a compressive strength of 270 MPa for a cast D.S.P. material. The tensile strength of such a product is about one tenth of the compressive strength.

Without reinforcement, the new materials are distinctly brittle with a linear stress–strain curve right up to the point of failure. The very dense microstructure of the D.S.P. binder, however, makes it particularly suitable for mechanical anchoring of thin fibres, which are not normally very firmly fixed in ordinary cement paste. The addition of such fibres gives the strong, brittle D.S.P. matrix a high degree of ductility (Bache 1981).

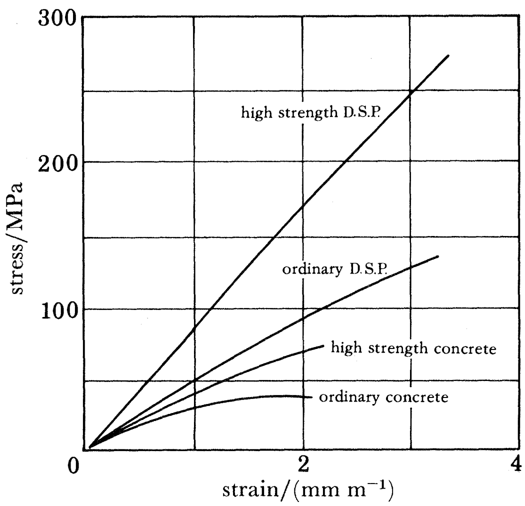

FIGURE 2. Stress–strain diagrams for ordinary concrete and D.S.P. materials.

Although the compressive strength is high, it is still only half of the strength of high quality structural steel. The density of the steel, however, is three times that of the D.S.P. materials, thus the strength:density ratio for D.S.P. materials is excitingly high. With the development of D.S.P. materials, we may have the means of building far bigger structures (bridges and towers) than has hitherto been possible.

Electron microscope observations reveal that D.S.P. materials have a very compact and dense microstructure. The addition of microsilica to cement paste is known to change the pore size distribution of such materials considerably towards finer pores (Sellevold *et al.* 1982), and a variety of observations confirm the extremely fine pore structure of D.S.P. binders.

Preece *et al.* (1982) found no freezable water in D.S.P. binders down to temperatures as low as -35 °C, and they found the Cl^- diffusion coefficient to be more than one order of magnitude lower than that of cement paste. Arup (1980) found the electrical resistivity of D.S.P. materials at 100% r.h. to be about 10^4 Ω m, which is 2–3 orders of magnitude greater than that of cement mortar, and close to the resistivity required for electric insulators.

APPLICATION OF D.S.P. MATERIALS

Although the first D.S.P. materials were made in the laboratory only five years ago, and although the properties of these materials are not yet fully established, the materials have already been used in practice for a range of purposes. Patent applications for D.S.P. materials and products are pending in several countries, and the D.S.P. materials and D.S.P. products are marketed by Densit A/S, Denmark, and Elborg Technology Company, U.S.A.

The earliest applications were overlays to concrete that was exposed to various types of aggressive environment, for example floors in chemical industries, parking areas and balconies. As liquid flow and the rate of ion diffusion are considerably reduced in these materials, deterioration by mechanisms that involve mass transfer is correspondingly decreased. Subsequently, more sophisticated applications of D.S.P. materials were attempted. In particular, the high abrasion-resistance of D.S.P. materials that use calcined bauxite as aggregates, has been utilized in materials that substitute cast basalt, rubber and steel as lining materials. Figure 3 shows a screw for feeding fly-ash into the pneumatic powder-transfer system at a cement plant. Such screws are normally made out of steel covered with sintered carbide. The steel screw is normally worn out within 250 h, whereas a similar screw, cast in D.S.P. material, had a service life that was five times longer.

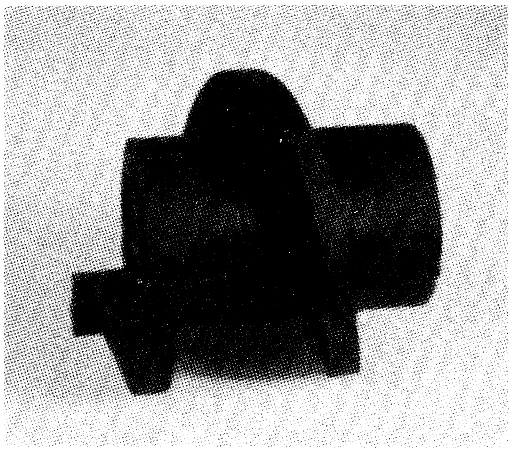

FIGURE 3. Screw cast in D.S.P. material.

Cast D.S.P. material is able to reproduce a surface geometry exactly while retaining high mechanical strength. D.S.P. materials are therefore used for press tools for pressure-shaping steel plates in the car body industry. The tools are made by simple casting methods at room temperature, with the original body parts as formwork.

CONCLUSION

Owing to suitable physical properties combined with simple processing techniques and low energy consumption, the D.S.P. materials have substituted successfully for cast basalt, ceramics, polymers, cast iron, steel, brass and other metals, in a wide variety of applications. The development of the D.S.P. materials is one example among others (Birchall *et al.* 1981), which illustrates that we are far from fully utilizing the large potentials of 'today's cements'. Exploitations have started, however, and we may already consider cement as an almost unlimited source for making inorganic products by a low-temperature technology, in competition with the high-temperature solidification technology of metals and with the resource-deficient technology of organic plastics. The development further suggests that fundamental studies and application of results from colloidal science, silicate chemistry, and the chemistry of highly concentrated and highly alkaline solutions, may gradually create the cement of tomorrow, which may be the basic raw material for a wide range of products in the future, thereby instituting a 'silica-age'.

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Discussion

N. McN. Alford (*I.C.I., The Heath, Runcorn, Cheshire, U.K.*). I should like to ask what the fracture energy is of Dr Hjorth's material.

L. Hjorth. The D.S.P. binder as such is brittle. Fibre-reinforced D.S.P. materials, however, are ductile. A fracture energy of 9 kJ/m² has been measured on samples of extruded D.S.P. materials with 4% (by volume) of 6 mm special polypropylene fibres.

R. J. Mangabhai (*Department of Chemistry, University of Salford, U.K.*). Has Dr Hjorth measured the mechanical properties of D.S.P. material at 8 °C and does the material set within 24 h? How long does the material have to be mixed for? With a high amount of Irgament Mighty is any retardation observed? Has Dr Hjorth done any rheological tests at 8 °C?

L. Hjorth. My group has no information on the properties of our materials at 8 °C. The mixing time varies with the composition of the D.S.P. material, and the type of mixer used. Intense mixing is required in order to obtain high quality products. High amounts of Irgament Mighty give retardation.

Sir Peter Hirsch, F.R.S. (*Department of Metallurgy and Science of Materials, University of Oxford*). Why is the tensile strength of Dr Hjorth's material so relatively low, i.e. one tenth of the compressive strength, if he has removed all the pores?

L. Hjorth. My group have changed the pore size distribution towards much finer pores, and reduced the total porosity, but have not removed all the pores.

G. K. Moir (*Blue Circle Industries p.l.c., Greenhithe, Kent, U.K.*). What are the curing conditions employed for a cast specimen such as the screw shown? In particular what is the temperature and duration of curing?

L. Hjorth. Accelerated curing at elevated temperatures (80 °C) is sometimes used in laboratory experiments to accelerate development programs. Industrial products, however, are normally cured at ordinary curing temperatures (20 °C) for a few days or weeks depending on the application.

S. A. Jefferis (*Civil Engineering Department, King's College London, U.K.*). In his last diagram Dr Hjorth showed a number of centrifugal pump impellers made from D.S.P. material. Can he say whether these can resist solutions that are normally detrimental to concrete, such as sulphate waters etc.?

L. Hjorth. Owing to the very fine pore structure of the D.S.P. materials the penetration of harmful ions, such as the sulphate ion, is very much restricted. The D.S.P. materials are still cement-based and they are therefore not inert to such ions. The service lifetime of the products in use, however, is very often sufficient to make them attractive.

R. Blundell (*Taylor Woodrow Research Laboratory, Southall, Middlesex, U.K.*). I was very interested to hear that the chloride ion diffusion coefficient is reduced by one order of magnitude compared with ordinary Portland cement concrete. Can Dr Hjorth confirm whether this can be achieved on site, as it appears to me that this material could have particular application to the repair of coastal and offshore structures where the diffusion of Cl^- ions is causing corrosion of embedded steel.

L. Hjorth. Although D.S.P. materials have already been used as described by Mr Blundell, we have not measured the rate of Cl^- penetration in such structures, mainly because the laboratory data are so convincing.

A. Kelly, F.R.S. (*University of Surrey, U.K.*). I really must congratulate Dr Hjorth upon a superb talk. It's so nice to see the ideas accepted of the advantage of low temperature forming of inorganics. Dr Hjorth mentioned fibres only in passing. What fibres have been added? What volume fractions of fibres?

L. Hjorth. Although the high strength D.S.P. materials demand high quality fibres and high fibre concentrations, my group have examined a variety of fibres and fibre concentrations. For instance, products have been made with 4% (by volume) of 6 mm special polypropylene fibres, and with 6% (by volume) of 6 mm steel fibres.

C. Defossé (*Dowell-Schlumberger Research and Development, Z. I. Molina La Chazotte BP* 90, *F*-42003, *Saint-Etienne Cedex, France*). Can Dr Hjorth, at the limit, make his paste pumpable? And if so, what are the best figures for plastic viscosity and yield value, on the assumption of a Bingham model?

L. Hjorth. The products can be made and have been made pumpable in practice. I have no figures for the rheological properties.

K. S. W. Sing (*Department of Chemistry, Brunel University, Uxbridge, U.K.*). I should like to ask Dr Hjorth whether different grades of finely divided silica have been used to prepare high-density cement-based materials and if so what differences there are in their behaviour.

L. Hjorth. My group have been working with various types of microsilica from various ferro-silicon plants, and we have also worked with more expensive products, such as Aerosil. By making allowance for the differences of the products, it has been possible to make good D.S.P. materials from most of them.

F. Massazza (*Italcementi Sp. A, Via Camozzi* 124, 24100 *Bergamo, Italy*). Does Dr Hjorth use special superplasticizers or high quantities of them, or both, to obtain such excellent results?

L. Hjorth. Most of the superplasticizers available on the market may be used. The amount of superplasticizers to be used depends on the type of D.S.P. material and the type of super-plasticizers, high dosages, however, are very often used.

J. Bensted (*Blue Circle Industries p.l.c., Greenhithe, Kent, U.K.*). Has Dr Hjorth experienced any durability problems with his product, bearing in mind the low water/cement ratio and organic content, in wet enviroments?

L. Hjorth. D.S.P. materials have been stored in water for five years without showing any sign of deterioration.

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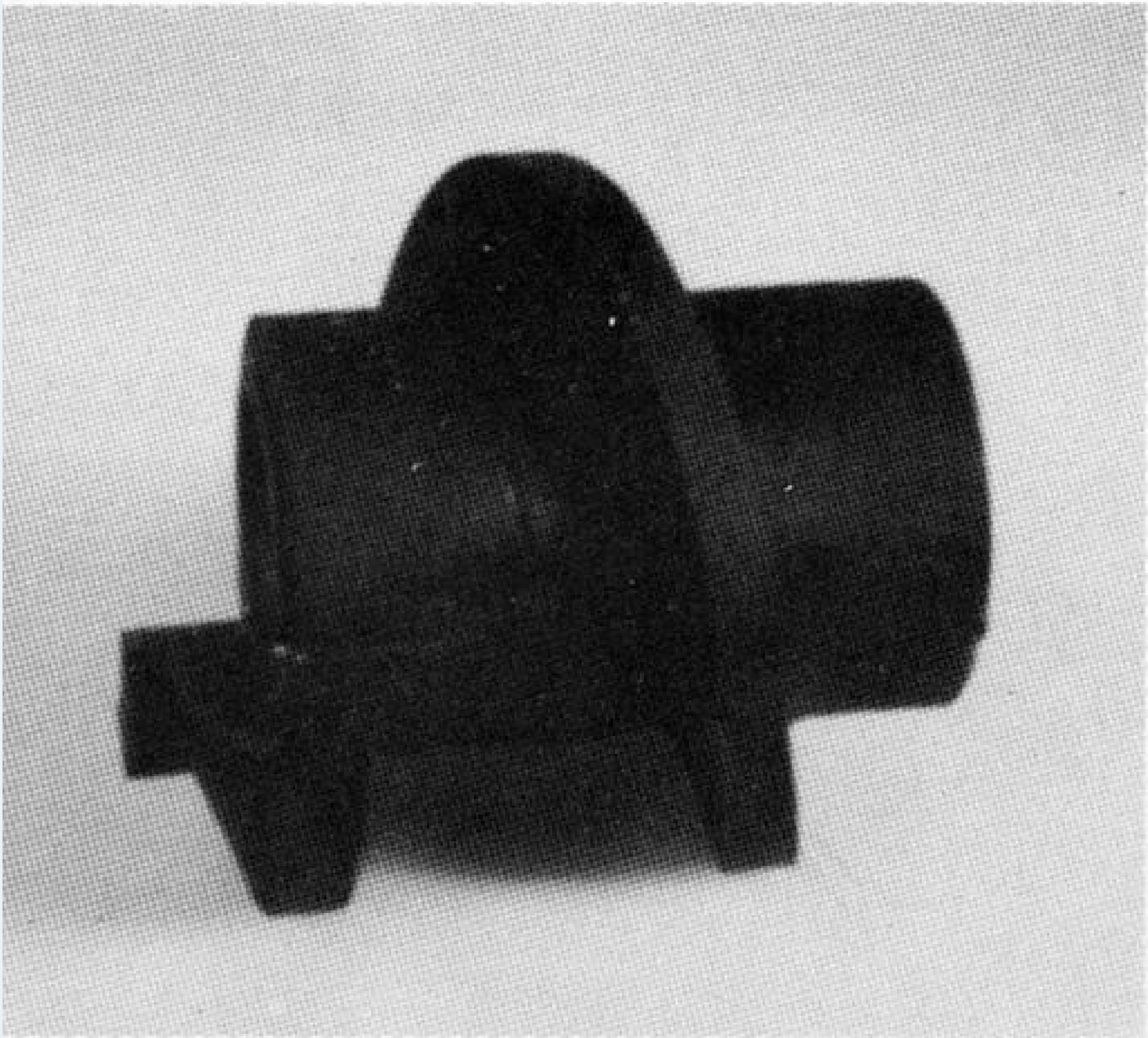

FIGURE 3. Screw cast in D.S.P. material.

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