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

Advanced Materials from Hydraulic Cements [and Discussion]

S. R. Tan, A. J. Howard, J. D. Birchall, C. D. Ellis, P. R. Marks, R. W. Cahn and J. H. Westbrook

Phil. Trans. R. Soc. Lond. A 1987 **322**, 479-491
doi: 10.1098/rsta.1987.0066

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

Phil. Trans. R. Soc. Lond. A **322**, 479–491 (1987)
Printed in Great Britain

Advanced materials from hydraulic cements

By S. R. Tan, A. J. Howard and J. D. Birchall, F.R.S.
Imperial Chemical Industries plc, New Science Group, Runcorn, Cheshire WA7 4QE, U.K.

[Plate 1]

Hydraulic cements are energy-cheap relative to other common materials and this was the driving force that led to the development of macrodefect-free (MDF) cements in 1981. In this paper the scientific principles of such materials in terms of porosity, particle packing and rheology are demonstrated and the use of a range of different cement types will be reviewed. The role of the polymeric rheological aid is emphasized and distinguished from that of so-called super-plasticizers used with conventional cements. The distinction between MDF cements and polymer concretes of various types is highlighted and the similarity of MDF cements and chemically bonded ceramics (CBCS) when the polymer is removed is noted. Various properties of MDF cements are given with emphasis on their high degree of mechanical reliability. These properties place MDF cements in a unique position in the materials field, a position that makes the replacement of hitherto more advanced engineering materials, such as metals, polymers and ceramics, a viable proposition. Areas of use are discussed.

INTRODUCTION

The oil crisis of the 1970s sharply heightened the awareness of energy costs associated with the winning and refining of raw materials and their subsequent processing into finished goods. The present fall in the price of oil can only be regarded as temporary and in the long term, energy costs will remain an important consideration in manufacture. Table 1 shows the approximate values of the energy costs per unit volume of some engineering materials in common use. Also shown in table 1 are the Young modulus of elasticity, the flexural strength and approximate values of fracture toughness, three properties of vital importance in any engineering material.

TABLE 1. PROPERTIES AND ENERGY COSTS OF SOME COMMON ENGINEERING MATERIALS

(After Alford *et al.* (1984).)

material	density 10^3 kg m^{-3}	Young modulus GPa	flexural strength MPa	fracture energy J m^{-2}	energy cost per unit volume relative to that of cement
wood	0.7	10	10–100	10^5	< 1.0
Portland cement	2.4	20	5	20	1.0
flat glass	2.5	70	100	10	3.0
PVC[1]	1.4	3	100	10^3	3.8
LDPE[2]	0.9	0.2	20	10^5	4.2
PS[3]	1.1	2	70	10^3	6.0
steel	7.8	205	500	10^6	19.2
stainless steel	7.8	205	500	10^6	28.8
aluminium	2.8	70	150	10^6	31.8

1. Poly(vinylchloride); 2. low density poly(ethylene); 3. poly(styrene).

Examination of table 1 reveals that hydraulic cements are energy-cheap. On average, the manufacture of cement requires only one tenth of the energy expenditure for the production of plastics and one twentieth of that required for energy-profligate metals (Birchall *et al.* 1983). In addition, the common cements are made from the most abundant elemental constituents of the Earth's crust, silicon and aluminium (as oxides) and the sulphate and carbonate of calcium. The low-energy content of cement-based materials relative to plastics and metals is not their only attraction, as has been noted (Birchall 1983). The increasing demand for incombustibility in a wide range of applications will only be met by materials that are non-carbon based.

The major deficiencies of hydraulic cement pastes are their low tensile or bending strength and their low toughness (see table 1). These have precluded their use as engineering materials except where the design is such that they are used only in compression. Numerous empirical relations between total pore volume and compressive strength have been developed (see, for instance, Feret 1897; Powers 1960). However, it was not until lessons were taken from the apparently unrelated fields of ceramics and biogenic minerals, that it was shown (Birchall *et al.* 1981 *a*, *b*) that the major factor governing the flexural or tensile strength of hardened cement pastes is the size of the macropores resulting from poor particle packing and air occlusion; similarly, it has been shown (Birchall *et al.* 1982; Kendall *et al.* 1983) that the incorporation of an organic matrix within the cementitious structure (as in a biogenic material) can significantly enhance the toughness of the material.

IMPROVING THE STRENGTH OF CEMENT PASTES

Porosity, rheology and particle packing

The weakness of cement paste is associated with porosity and this may be reduced in a number of ways. One of these is to impregnate the hardened cement paste with an organic monomer, which is then polymerized (Swamy 1979). This leads to a quadrupling of tensile strengths (to 12 MPa) and a doubling of modulus. Another is to reduce the water content of the mix by adding a small amount of a surfactant such as a sulphonated naphthalene condensate. This leads to dispersion of the cement grains, maintenance of good rheology at a lower water content and produces a twofold increase in compressive strength (Hattori 1978). Alternatively, napthalene sulphonates may be used in conjunction with fine silica (Bache 1981; Hjorth 1983) to modify the pore structure of the hardened cement paste. The compressive strength of such materials is high (more than 100 MPa), but the tensile strength is still low as macropores remain.

In another approach, pressure can be used to expel water from the mix and push the cement grains closer together. Roy & Gouda (1973) found that the use of a compaction pressure of 345 MPa leads to a low porosity level (2 vol. %) and significantly improved mechanical properties: an indirect tensile strength of 64 MPa and a compressive strength of 655 MPa.

However, such techniques do not lend themselves to the production of large or complicated shapes and it was not until recently that it was found that by the addition of a water-soluble polymer, the use of high shear mixing and the application of a modest pressure (*ca.* 5 MPa), cement pastes of high bending strengths could be produced in complex shapes with great facility (Birchall *et al.* 1981 *a*, 1982). The water-soluble polymer with high molecular mass acts as a rheological aid and reduces the interparticle friction coefficient, which usually prevents particulate rearrangement from occurring in concentrated suspensions. It also increases the viscosity of the mix significantly, thus permitting the use of intensive high-shear mixing processes (such as twin-roll milling and mix-extrusion) without inducing cavitation. Hence aggregates of cement powder can be broken down to individual particles, which can then be repacked in a near-optimum configuration. In consequence, cement pastes containing volume fractions of cement particles greater than 0.7 are routinely obtained. These pastes, in their uncured state, are stiff doughs, which behave as truly plastic bodies having low yield stresses (Kendall *et al.* 1983). This makes moulding of intricate shapes easy, requiring only modest pressures. Also, the air in the pastes obeys Boyle's Law and is easily removed from the mouldings at these low pressures, thus eliminating porosity. The final, densified materials contain no macroporosity and the polymer resides at the interface between the close-packed cement grains, intimately combined with the hydration products, as shown in figure 1, plate 1. In this way they resemble inorganic materials of biological origin, such as mother-of-pearl (nacre) (Birchall 1983, 1984).

The essence of the approach by Birchall *et al.* (1981*b*) was to assume that cement pastes, in exhibiting brittle fracture characteristics, behave according to the equation derived by Griffith (1920),

$$\sigma = (ER/\pi c)^{\frac{1}{2}},$$

where σ is the tensile or bending strength, E is Young's modulus, R is fracture energy and c the length of a crack-like pore. They found that the strength of a normal cement paste is restricted by the presence of macroscopic voids and that by removing these, bending strengths of up to 70 MPa could be obtained. Their results were confirmed by Alford *et al.* (1982) and Eden & Bailey (1984*b*). Further, Kendall and co-workers (1983) have shown that by using a combination of high-alumina cement and a copolymer of vinyl acetate and vinyl alcohol, strengths up to 150 MPa may be achieved with this approach.

The application of the Griffith equation to cement pastes has been controversial for some time (see, for instance, Kaplan 1961; Brown & Pomeroy 1973; Higgins & Bailey 1976; Alford *et al.* 1982). Mindess (1983) recently reviewed the subject and concluded that the weight of evidence supports the application of linear elastic fracture mechanics to hardened cement pastes, but perhaps not mortar or concrete. There is no doubt that the concept of flaw size in very porous materials such as cement pastes is complex and makes the interpretation of strength more difficult. Nevertheless, Kendall *et al.* (1983) derived a modification of the Griffith equation, which showed good agreement with experimental results obtained from both hardened cement pastes and a porous silica glass model system. Recently Swift *et al.* (1986) concluded that the equation derived by Kendall *et al.* could also be used to describe the mechanical properties of cement-based mortars.

It has been suggested (Eden & Bailey 1984*a*, *b*) that the high-strength of macrodefect-free (MDF) cements† is mainly because of the presence of the organic polymer. Kendall & Birchall (1985) have shown that MDF cement pastes containing only cement and water can exhibit strengths up to 80 MPa in conjunction with a modulus of 75 GPa and porosity of less than 1%. Such polymer-free materials are significantly more brittle than MDF cement pastes

---

† MDF cements are pastes of hydraulic cement and water to which a small amount of a water-soluble polymer has been added. This, combined with high shear mixing and the application of a modest pressure (*ca.* 5 MPa) leads to the production of pastes having flaw sizes less than 0.1 mm and concomitant high strength.

containing poly(vinylalcohol/acetate), where the high fracture energies (up to 160 J m^{-2}) are acknowledged to be due, in some part, to chemical interactions between the cement and polymer.

Because the properties of MDF cement pastes differ so significantly from conventional cementitious solids, the term 'new inorganic materials' (NIMS) was coined to describe them.

Processing routes to the production of NIMS

Two distinct processing routes have been developed that lead to the production of NIMS: twin-roll milling plus pressing and mix-extrusion.

In the twin-roll milling process, the constituents, cement, polymer and water, are premixed to form a dry granular 'crumble' with an orbital mixer or ribbon blender. This granular material is fed onto the rolls of a twin-roll mill, which are chilled to retard the chemical reactions responsible for hardening. A cohesive dough with the consistency of soft rubber is rapidly formed. At this stage the dough contains some occluded air and the volume fraction of cement particles is about 0.6. The sheet is removed from the mill and can then be moulded to the required shape by using low pressures (no more than 5 MPa). At these pressures, the volume of occluded air is markedly reduced and the volume fraction of cement particles is thus increased. The object becomes hard as a result of inorganic hydration reactions, which may be accelerated by the application of heat. The deformability of the dough decreases as setting proceeds and air pockets are not reformed on release of the pressure. Any air remaining in the residual microscopic porosity escape by slow diffusion through the body until equilibrium pressure is reached within the pore.

For the calcium aluminate cement–poly(vinylacetate/alcohol)–water system there is then a post-forming volume contraction of 8–10% with the result that the volume fraction of cement particles is again increased. Porosity measurements indicate that the volume fraction of particles is about 0.8 and the final porosity volume fraction is 0.01 or less.

The mix–extrusion process for NIMS uses the same principles of high shear mixing and exclusion of air, but in this case the air is excluded at the outset by carrying out mixing operations under vacuum. The polymer may be added as a powder with the water being added to an evacuated premixture of cement and polymer. Alternatively the polymer may be premixed with the water to form a gel, the gel being evacuated to remove air before being mixed under vacuum with the cement powder.

For either, the extrudate contains essentially no air and thus the components manufactured do not require the subsequent pressing step used in the twin-roll milling process. Hardening again occurs as a result of hydration reactions and, for the calcium aluminate cement-poly(vinylacetate/alcohol)–water system there is the post-forming contraction.

Scope of application of NIMS processing

The techniques described by Birchall *et al.* (1981 *a*, 1982) can be applied to any cementitious material. The aqueous chemistry of the cement and the nature of the polymer will have a significant influence on the rheological behaviour of the cement–polymer–water system. It is essential that the polymer is capable of strong attachment to the particles with trains of polymer extending into the aqueous phase (Birchall 1983). Equally, the polymer must be compatible with the high pH and ionic strength of the cement aqueous phase and must not be prematurely precipitated by reaction with dissolved species derived from the cement (Birchall 1983). For this reason, in processing ordinary Portland cements (OPC) compositions, a polymer such as hydroxypropylmethyl cellulose (HPMC) is preferred to poly(vinylalcohol/acetate) (PVA/Ac) because the latter undergoes rapid hydrolysis because of the high pH and precipitates from solution. Although OPC + PVA/Ac NIMS have good mechanical properties, processability is limited when compared with similar materials made with HPMC.

Calcium silicate-based NIMS materials have also been made with α-dicalcium silicate (α-C_2S)† (Takagi *et al.* 1984). These materials exploit the fact that dicalcium silicates are less alkaline than tricalcium silicate (the major constituent of OPC) and consequently their reaction with water is slower. Indeed, α-C_2S does not hydrate and harden if water is added at normal temperature, but requires hydrothermal treatment. Consequently α-C_2S cement may be produced with NIMS processing techniques without regard to polymer type, other than that it should confer the appropriate rheological characteristics to the mix.

Articles may be moulded to shape, dried and then cured in an autoclave to yield the final set product. The materials are notably stable in the presence of water.

Calcium sulphate-based cements can also be processed by NIMS techniques to give high-strength cement pastes (Birchall *et al.* 1981 *b*). However, retarders may have to be used to prevent premature setting.

Calcium aluminate-based NIMS materials can also be made by using a variety of polymeric rheological aids, but when poly(vinylalcohol/acetate) is used, the interaction between the cement particles and polymer is especially strong. Rodger *et al.* (1985) have suggested that this is due to a reaction between the aluminate ion $[Al(OH)_4]^-$ and hydroxyl groups in a manner analogous to the reaction known to occur between the borate ion $[B(OH)_4]^-$ and hydroxyl groups (Pritchard 1970). However, it is more likely that in the process of condensation which brings about the precipitation of $Al(OH)_3$, the polymer is integrated into the structure of the hydroxide by the coordination of its hydroxyl groups. This strong bonding allows high shear mixing to take place, associated with a genuinely plastic rheology. A post-forming volume contraction of 8–10% occurs on drying (Birchall 1983; Kendall *et al.* 1983). This appears to result from the contraction of the extended polymer chains that interconnect the cement particles as the polymer dehydrates and results in the collapse of colloidal porosity. The net result is that in this particular system, the final porosity volume is 0.01 or less, much lower than other NIMS cements where colloidal porosity remains.

PROPERTIES OF NIMS CEMENTS

The detailed properties of NIMS cements are dependant on the exact cement–polymer system being used. However, there is a major distinction between the properties of those cement pastes based on the high-alumina cement–poly(vinylalcohol/acetate) system and all other cement–polymer combinations. All the latter lead to hardened pastes with properties similar to those described by Birchall *et al.* (1981 *a*, *b*), namely flexural strength 60–70 MPa, Young's modulus *ca.* 40 GPa, compressive strength greater than 200 MPa and residual porosity 10–15 vol. %. The former have significantly higher mechanical properties as shown in table 2 and for this reason have been pursued.

---

† Conventional cement chemistry notation; C is CaO and S is SiO_2.

Table 2. Properties of NIMS cements

high-alumina cement: poly(vinylalcohol/acetate) system

flexural strength	150–200 MPa
Young's modulus	40–50 GPa
compressive strength	380 MPa
impact strength (unnotched Charpy)	3 kJ m^{-2}
fracture energy	200–500 J m^{-2}
Poisson's ratio	0.2
Weibull modulus	20–40
hardness	100–110 VPN (Vickers pyramidal number)
density	2500 kg m^{-3}
porosity	1 % vol.
permeability (oxygen)	10^{-6} mol/ms^{-1} Pa^{-1}
thermal expansion (25–100 °C)	9.7×10^{-6}/K
thermal conductivity (25–100 °C)	1 W m^{-1} K^{-1}
volume resistivity	10^{9}–10^{12} Ω cm
discharge inception voltage	10 kV
electric strength	9 kV mm^{-1}
dielectric strength (1–10 kHz)	9
acoustic tan δ	0.1
Q factor	40

Table 2 has been divided into three sections, which give some mechanical, physical, electrical and acoustic data. The table is self-explanatory, but attention is drawn to some of the more unusual properties of calcium aluminate-based NIMS cements.

Strength and Weibull modulus

The bending strength of NIMS cement is at least an order of magnitude higher than ordinary cement paste and approaches that of common engineering materials such as aluminium, filled polymers and ceramics. The strength properties of NIMS are highly reproducible and figure 2 shows a Weibull plot of strength. The Weibull Modulus, m, given by the slope of the plot is

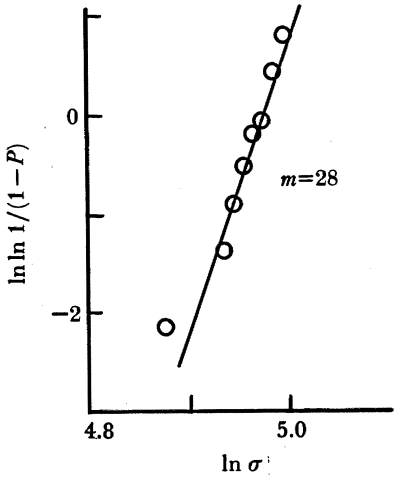

Figure 2. Weibull plot for NIMS cement. P is the failure probability and σ the flexural strength in megapascals. $m = 28$.

28, significantly higher than that for ordinary cement pastes (Kendall *et al.* 1986). The poor mechanical reliability of advanced ceramics is recognized to be one factor limiting more widespread use of these materials (Rice 1984). Significant improvements are strenuously sought after as a step towards the use of advanced ceramics in engineering applications. To date they have not been achieved without the use of proof-testing and non-destructive examination to reject the weak samples. NIMS cements exhibit high Weibull moduli without resorting to any sample selection procedures, reflecting the refinements in processing that have been achieved.

The fracture energy of NIMS is intermediate between that of essentially brittle materials such as glass or ceramics and ductile materials such as polymer and metals. In engineering terms it approximates in toughness to grey cast iron. Alford & Birchall (1985) have shown that, by incorporation of fibres, the work of fracture can be significantly increased. With *ca.* 15 vol. % of nylon fibres incorporated in the matrix, the impact toughness is increased from 5 to 120 kJ m^{-2}. This compares well with fibre-reinforced thermosets that have unnotched Charpy impact energies of around 100 kJ m^{-2} (Orton *et al.* 1984).

ELECTRICAL

The electrical properties of NIMS cements are such that they may be used in low-tension applications. An interesting property of the material is its resistance to arcing and the lack of carbonaceous product when an arc is finally struck. This results in a comparative tracking index of greater than 1000 when tested according to BS5901. The dielectric constant of calcium aluminate NIMS cements can be as low as seven with a dissipation factor of 0.015. These properties together with the low temperature required in processing, are of interest in electronic substrates, packaging, etc. (Chandrashekar *et al.* 1986; Perez & Roy 1986).

APPLICATIONS

NIMS cements provide combinations of properties not generally associated with cement-based materials and some properties may, indeed, be unique. The MDF process described above allows the addition of fibrous and particulate fillers with the result that properties may, within certain limits, be tailored to suit specific applications. For this reason it is probable that NIMS cements will not initially be used in high-volume applications, but in areas where volume may be low, although added value is high. As such, NIMS may be regarded as advanced materials with properties that either are unique, or make comparison with metals, plastics and ceramics a tenable proposition.

The potential applications for NIMS cements are legion and have been reviewed by Alford *et al.* (1984), Alford & Birchall (1985). Three possible areas that exploit the special characteristics of NIMS are given below, but it should be made clear that these are but a few of the total number.

ACOUSTICS

In recent years, the increasingly stringent regulations governing noise pollution have led acoustic properties to be taken into consideration when selecting materials. In general, low-modulus materials exhibit high damping ($\tan \delta$) characteristics, whereas in high-modulus

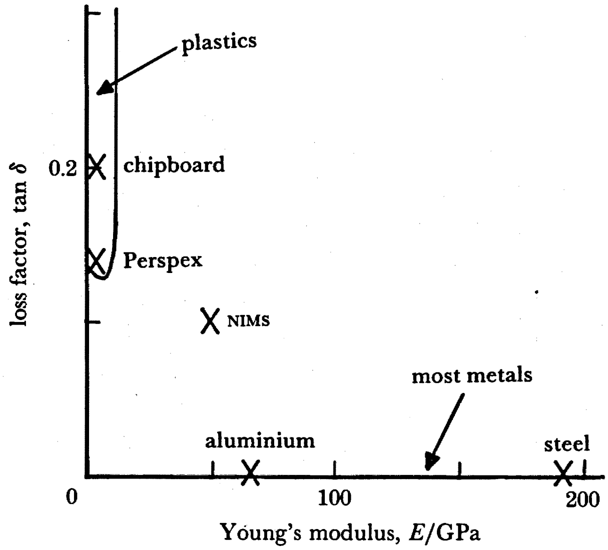

FIGURE 3. Loss factor, tan δ, and the Young modulus, E, for various materials (after Alford & Birchall 1985).

materials, tan δ is low (figure 3). This can cause problems where heavy machinery must be supported or where the deflection under load must be small. NIMS cements are both acoustically damping ($\tan\delta = 0.1$) and have high Young moduli (40–50 GPa). Potential applications therefore, include use as supports for medical X-ray or laser equipment, where vibrations from an external source can cause loss of resolution. Noise reduction applications in the automotive field have been suggested and the use of NIMS cements for valve gear assembly covers is being investigated (M. Love, personal communication).

It has also proved possible to manufacture effective loudspeaker enclosures with NIMS cements (Alford & Birchall 1985). So far, these have merely exploited the attractive damping characteristics of the materials. However, NIMS cements can easily be moulded into complex shapes and it is interesting to speculate on what improvements in acoustic performance might be obtained from a rigid, strong, highly damping, but non-tetragonal enclosure.

ARMOUR

Other than sheet steel, almost all armour systems used to protect personnel, vehicles or buildings are composites to maximize ballistic protection while minimizing mass. They usually consist of a strong but brittle, hard-face material backed by a tough, deformable spall shield. The ballistic limit is often defined as the velocity of the projectile at which no fragmentation or spalling occurs on the back face of the composite, although significant damage may be sustained by the front face. Alternatively, the concept of residual velocity or momentum may be used, wherein a zero value signifies no penetration or spalling of the armour system. The areal density of the sample under test is usually given when quoting ballistic limit data because performance can be improved by increasing the armour thickness, but only with an increase in mass.

Ceramics have been used in conjunction with a fibrous spall shield for some time (Cook 1970) and boron carbide has become the standard hard-face material by which others are judged.

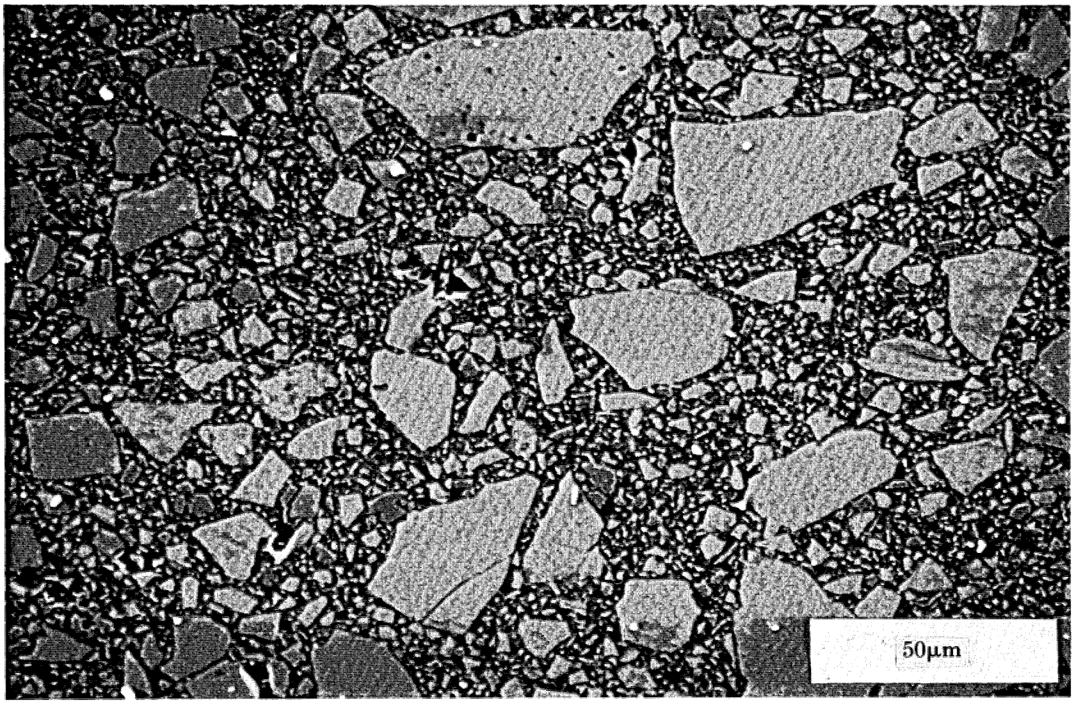

FIGURE 1. Microstructure of NIMS (calcium aluminate) cement.

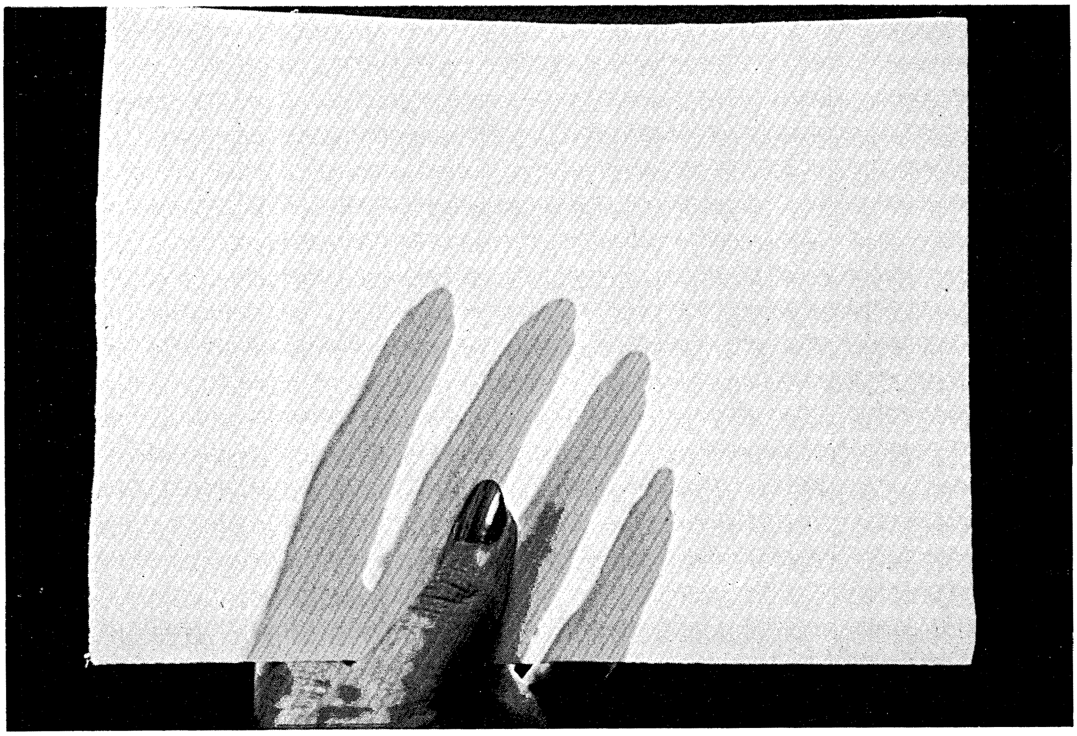

FIGURE 4. Sheet of NIMS cement: thickness 250 μm.

The spall shield, which 'catches' the shattered fragments of hard-face material together with the deformed projectile, may be Kevlar-, nylon-, steel-, aluminium- or glass-reinforced plastic. The properties of the ceramic material that are generally considered to be desirable are high Young's modulus and hardness. Table 3 shows the properties of two ceramics commonly used as armour and compares them with NIMS cement.

TABLE 3. CERAMIC FACING MATERIALS

(After Alford & Birchall (1985).)

	boron carbide	alumina	NIMS
density/(kg m^{-3})	2500	3600	2400
hardness (Knoop)	3000	2500	100
bend strength/MPa	275	350	150
modulus/GPa	455	287	50
strain (%)	0.06	0.08	0.3
strain energy/(kJ m^{-3})	82.5	140	225

Although NIMS cement has a lower hardness and modulus than either boron carbide or alumina, it has a considerably higher strain energy and in tests, Alford & Birchall (1985) showed this to be of considerable benefit.

The processing characteristics of NIMS cements make the production, at low temperatures, of large, complicated mouldings easy. This is not so with ceramics. In addition, NIMS cement may be reinforced with polymer fibres – an impossibility with ceramics – and this confers the ability to withstand multiprojectile impacts. In consequence, Alford & Birchall (1985) have concluded that it is feasible to use NIMS cement with a suitable backing material to give a composite of areal density 25 kg m^{-2} that will defeat threats of about 750 ms^{-1} from either arms or fragmentation.

CRYOGENICS

The strength of most materials is enhanced at low temperature and this is true of some types of NIMS cements. However, body centred cubic (BCC) metals, which include iron, mild steel, tungsten and molybdenum have a tendency to form microcracks in the crystals at low temperatures and these can lead to catastrophic failure under stress. Some plastics, such as poly(vinylchloride) and nylon, suffer from embrittlement at cryogenic temperatures, thus offsetting the improved strength and Young modulus, which are more than doubled at 77 K.

In contrast to this behaviour, NIMS cements increase in flexural strength, Young's modulus and K_{Ic}, although the strain energy release rate, G_{Ic} decreases slightly as a consequence of the increased modulus. The net result is that the impact toughness of unnotched Charpy samples of NIMS cement is unchanged as the operating temperature is reduced from 300 to 77 K (Alford & Birchall 1985).

This insensitivity of impact toughness to low temperature when combined with its low thermal conductivity and permeability to gases (table 2) suggests a variety of cryogenic applications for NIMS.

The three application areas above demonstrate how the unusual combinations of properties available from NIMS cements may give rise to their application as advanced materials rather than the more common and conventional applications in which cements are normally found.

Other applications will undoubtedly exploit the ability to produce unusual forms of cement-based materials by the NIMS processing techniques. An interesting example of this is shown in figure 4, plate 1, which shows a sheet of NIMS cement that is a mere 250 μm in thickness and is translucent.

CEMENTS AS CHEMICALLY BONDED CERAMICS

The phrase 'chemically bonded ceramics' or 'CBCS' has recently been coined (R. Roy personal communication) and these have been defined by Birchall (1984) as describing 'densely-packed assemblies of ceramic particles, free from macroscopic voids, in which union between the grains is produced at temperatures far lower than those required in conventional [ceramics] technology'. It might be argued that conventional hydraulic cements were the first CBCS because they are inorganic solids in which the cement grains are ceramic particles and union between them is achieved via the hydraulic reaction. However, they are not free from macroscopic voids with the result that mechanical properties are poor. Birchall (1984) has suggested that MDF cements may be considered to be CBCS, but the purists among ceramists might disagree, because they contain a polymeric material. However, Kendall & Birchall (1985) have shown that totally inorganic derivatives of MDF cements can be made that have good mechanical and physical properties. These materials may be produced containing as little as 1 vol. % of porosity, all of which is less than a micrometre in size. As a result, flexural strengths of up to 80 MPa and a Young modulus of 75 GPa may be obtained. More recently, Kendall *et al.* (1986) have shown that these mechanical properties can be obtained while still retaining high values of Weibull modulus. This is illustrated in figure 5, which shows the poor strength and Weibull modulus of ordinary cement. This figure also shows the high Weibull modulus resulting from the use of NIMS processing. When the polymer is thermally removed from the NIMS cement, the flexural strength falls because of the reintroduction of porosity and flaws. Nevertheless, the high Weibull modulus is retained illustrating the uniformity of that porosity. After the material has been rehydrated and carefully dried, the flexural strength rises significantly and the Weibull modulus is unchanged. None of the process steps required to achieve these results requires

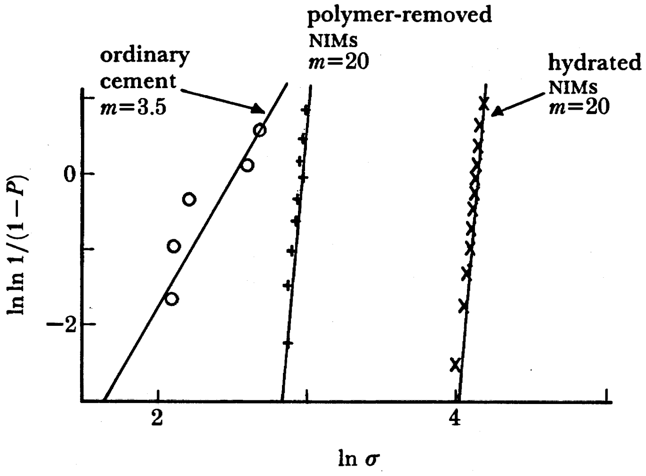

FIGURE 5. Weibull plot of strength for various cement pastes (after Kendall *et al.* 1986).

temperatures greater than 450 °C, significantly lower than those required in conventional ceramics technology. These materials, which are refractory ceramics, genuinely fit the definition of CBCS.

In creating NIMS cements the preconceptions of the properties of hardened cement pastes have had to be modified drastically over the past five years and cements can now assume a position in the hierarchy of materials hitherto considered impossible. This is a good illustration of what can be done when knowledge of microstructure–property relations is allied to close control of process technology. It highlights the need for close collaboration between the chemist, materials scientist and process engineer if the demand for improved materials for use in advanced applications in the 1990s is to be met.

REFERENCES

Alford, N. McN., Groves, G. W. & Double, D. D. 1982 *Cem. Concr. Res.* **12** (3), 349–358.

Alford, N. McN., Birchall, J. D., Howard, A. J. & Kendall, K. 1984 In *Proc. Conf. on Metals Engineering, University of Leeds, 10–12 July 1984*, pp. 73–79. Institution of Metallurgists.

Alford, N. McN. & Birchall, J. D. 1985 *Mater. Res. Soc. Symp. Proc.* **42**, 265–276.

Bache, H. H. 1981 Dense cement ultrafine particle-based material. In *Proc. 2nd Int. Symp. on Superplasticizers in Concrete, Ottowa, Canada.* Ontario: CANMET, Dept of Energy, Mines and Resources.

Birchall, J. D. 1983 *Phil. Trans. R. Soc. Lond* A**310**, 31–42.

Birchall, J. D. 1984 *Trans. J. Br. ceram. Soc.* **83** (6), 158–165.

Birchall, J. D., Howard, A. J. & Kendall, K. 1981*a* European Patent no. 0021682.

Birchall, J. D., Howard, A. J. & Kendall, K. 1981*b* *Nature, Lond.* **289**, 388–389.

Birchall, J. D., Howard, A. J. & Kendall, K. 1982 European Patent no. 0055035.

Birchall, J. D., Howard, A. J. & Kendall, K. 1983 *Metall. Mater Technologist* **15** (1), 35–38.

Brown, T. H. & Pomeroy, D. D. 1973 *Cem. Concr. Res.* **3** (4), 475–480.

Chandrashekar, G. V., Cooper, E. I. & Shafer, M. 1986 Electrical properties of MDF-type cements. *Am. Ceram. Soc., 88th annual meeting abstracts* **143**.

Cook, R. L. 1970 U.S. Patent no. 3509833.

Eden, N. B. & Bailey, J. E. 1984*a* *J. Mater. Sci.* **19**, 150–158.

Eden, N. B. & Bailey, J. E. 1984*b* *J. Mater. Sci.* **19**, 1677–2690.

Feret, R. 1897 *Bull. Soc. Encour. Ind. natn., Paris* **2**, 1604.

Hattori, K. 1978 In *Superplasticizers in concrete* (*Proc. Int. Symp. Ottowa, Canada, 29–31 May 1978*) (ed. V. M. Malhotra & T. A. Wheat), vol. 1, pp. 49–86.

Higgins, D. D. & Bailey, J. E. 1976 *J. Mater. Sci.* **11**, 1995–2003.

Hjorth, L. 1983 *Phil. Trans. R. Soc. Lond.* A**310**, 167–173.

Griffith, A. A. 1920 *Phil. Trans. R. Soc. Lond.* A**221**, 163–198.

Kaplan, F. M. 1961 *J. Amer. Concr. Inst.* **58**, 591–610.

Kendall, K., Howard, A. J. & Birchall, J. D. 1983 *Phil. Trans. R. Soc. Lond.* A**310**, 139–153.

Kendall, K. & Birchall, J. D. 1985 *Mater. Res. Soc. Symp. Proc.* **42**, 143–148.

Kendall, K., Alford, N. McN., Tan, S. R. & Birchall, J. D. 1986 *J. Mater. Res.* **1** (1), 120–123.

Mindess, S. 1983 Application of fracture mechanics to cement and concrete: a historical review. In *Fracture mechanics of concrete* (ed. F. H. Wittman), pp. 1–30. Amsterdam and New York: Elsevier Science Publishers.

Orton, M. L., Howard, R. D. & Spurr, W. I. 1984 Paper presented at Int. Conf. on Fibre Reinforced Composites, University of Liverpool, 3–5th April 1984.

Perez, M. & Roy, D. M. 1986 Cementitious Composite Materials with low dielectric permittivity. *Am. Ceram. Soc., 88th annual meeting abstracts*, **142**.

Powers, T. C. 1960 In *Proc. 4th Inst. Symp. Chemistry of Cement.* (National Bureau of Standards Monograph no. 43), vol. II, pp. 577–613. Washington, D.C.: NBS.

Pritchard, J. F. 1970 *Polyvinyl alcohol.* London: Gordon and Breach.

Rice, R. W. 1984 *J. Phys. Chem. Solids* **45** (10) 1033–1050.

Rodger, S. A., Brooks, S. A., Sinclair, W., Groves, G. W. & Dodds, D. D. 1985 *J. Mater. Sci.* **20**, 2853–2860.

Roy, D. M. & Gouda, G. R. 1973 *Cem. Concr. Res.* **3**, 807–820.

Swamy, R. N. 1979 *J. Mater. Sci.* **14**, 1521–1553.

Swift, D. S., Nicholas, D. M. & Scott, R. A. M. 1986 *Int. J. Cem. Compos. lightweight Concr.* **8** (1), 39–44.

Takagi, S., Yokota, N., Sato, S. & Nishi, T. 1984 U.K. Patent no. GB2140795A.

Discussion

C. D. Ellis (*Brunel University, U.K.*). As one who has been involved with building materials for most of my working life, I am pleased to see from the interesting paper by Dr Tan and his colleagues that cements are now becoming respectable engineering materials.

My close involvement with building materials, however, leads to an instinctive concern when high-alumina cement (HAC) is mentioned. For me, the phenomenon of 'conversion' is inextricably linked with that material. This is the process whereby HAC concretes (admittedly badly made ones) could suffer from porosity and strength loss as a result of a crystallin conversion of one of the main cementitious hydration products. This caused a number of failures in the mid-1970s and led to a ban on the use of HAC concrete for structural applications.

Could Dr Tan assure us that no such behaviour is displayed by his second-generation new inorganic material based on HAC.

S. R. Tan. My colleagues and I prefer not to offer 'assurance' that conversion cannot occur in second-generation NIMS based on HAC, as this could have unfortunate legal implications for the future! However, there are three pieces of evidence that would lead us to believe that conversion is unlikely.

1. XRD analysis generally fails to identify any crystalline hydrate products, certainly the deca- and hepta-hydrates. Indeed, only on very singular occasions has any crystalline hydrate been identified, and that has been the thermodynamically stable hexahydrate.
2. It is generally believed that conversion will not occur below water : cement ratios of about 0.22. Our compositions always use water : cement ratios below 0.14.
3. Beams of NIMS have been exposed to conditions of 95% relative humidity and 40 °C for three days, conditions that would normally lead to a catastrophic reduction in strength and, indeed, cracking, if conversion were taking place. This was not observed.

P. R. Marks (*Shell Research Limited, Thornton Research Centre, U.K.*). With respect to the comments on the effect of thermally removing the PVA from the high-alumina MDF materials, resulting in properties similar to the standard cement-based materials, would the authors like to comment further on the thermal capabilities of PVA-containing NIMS, with respect to creep and general mechanical degradation at high temperatures? In particular, could they give an indication of the maximum continuous temperatures and the maximum transient temperatures under which the materials might be expected to function effectively?

S. R. Tan. The maximum continuous operating temperature would be about 100 °C. Above this temperature, prolonged exposure will lead to a steady, and irreversible decline in strength and modulus, falling to a minimum when all the polymer has decomposed. The residual flexural strength, in the latter case, is of the order of 20 MPa. In terms of transient exposure, the only information we have relates to electrical arc testing whereby 1000 such arcs did not cause significant damage. The precise temperature and its duration is not known. However, one presumes that the temperature is of the order of thousands of degrees, and the duration measured in milliseconds or less.

R. W. Cahn (*Department of Metallurgy and Materials Science, University of Cambridge, U.K.*). The extremely interesting presentation by Dr Tan excites curiosity as to the precise mode of operation of the polymer additive. It would appear that the reduction of dilatancy and the reduction of porosity are intimately linked. What is the physical mechanism by which the polymer achieves these effects, and what physical features distinguish a polymer which is effective in these ways from one which is not? What determines the concentration of polymer needed?

S. R. Tan. Details of the way in which the polymer modifies the rheology of the cement–water mixture are to be found in the paper by Kendall *et al.* (1983).

J. H. Westbrook (*Knowledge Systems, New York, U.S.A.*). Much cement deterioration in northern climes is because of the freeze–thaw cycle and the presence of salt. Are the improved cements more resistant to this type of attack?

S. R. Tan. Freeze–thaw cycling of NIMS leads to some degradation in the flexural strength up to about 75 cycles. Further cycling has little effect. Throughout cycling the modulus is essentially unaffected, suggesting that the bulk of the material is not damaged by freeze–thaw and that the fall in flexural strength observed is due to surface effects.

The resistance of NIMS to salt has been tested both in terms of salt spray testing against ASTM B117–73 and also to sea water (standard mean ocean water). Apart from slight surface discolouration, NIMS was unaffected by either.

We have not examined the combined effects of freeze–thaw and salt on NIMS.

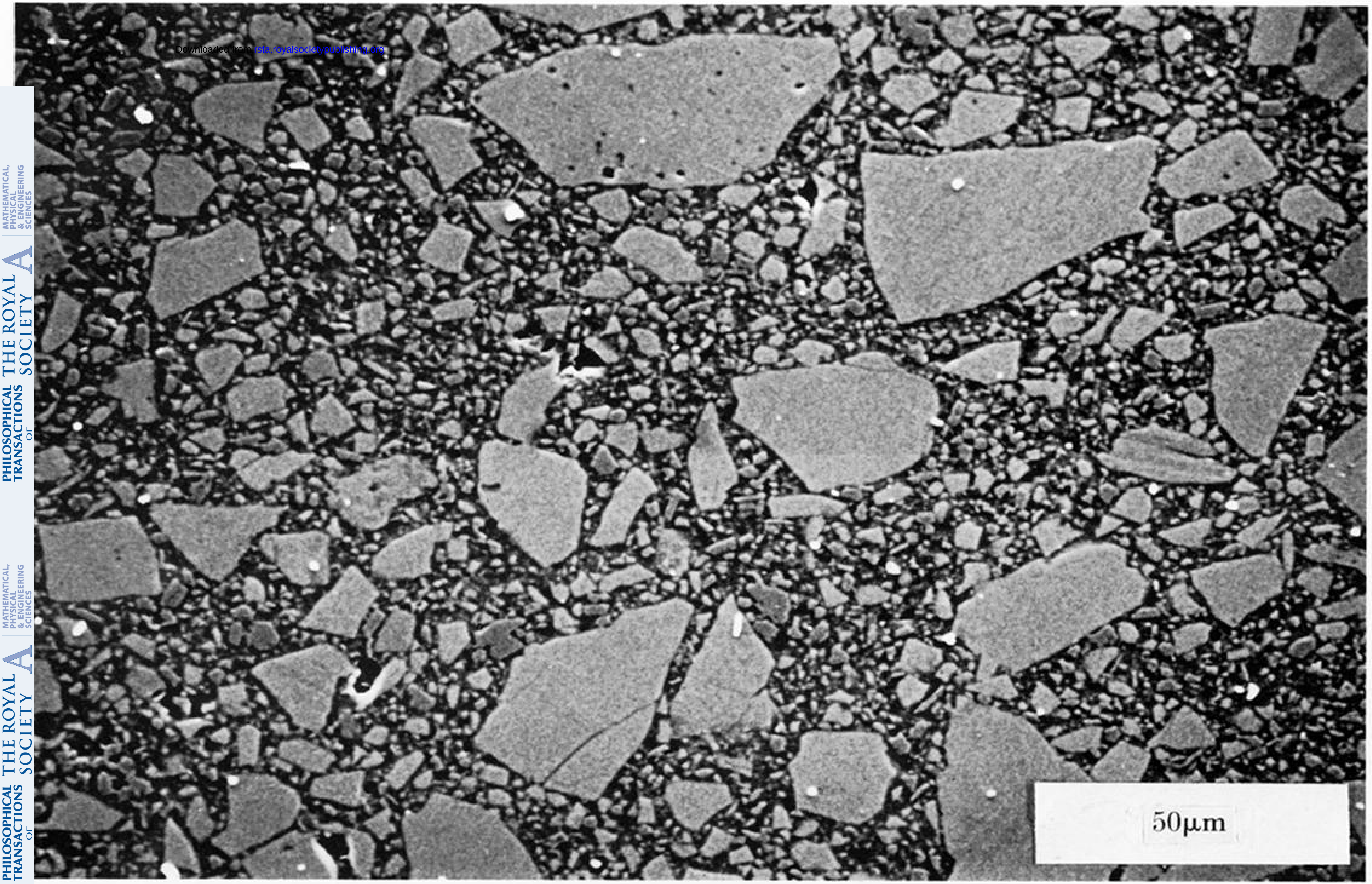

FIGURE 1. Microstructure of NIMS (calcium aluminate) cement.

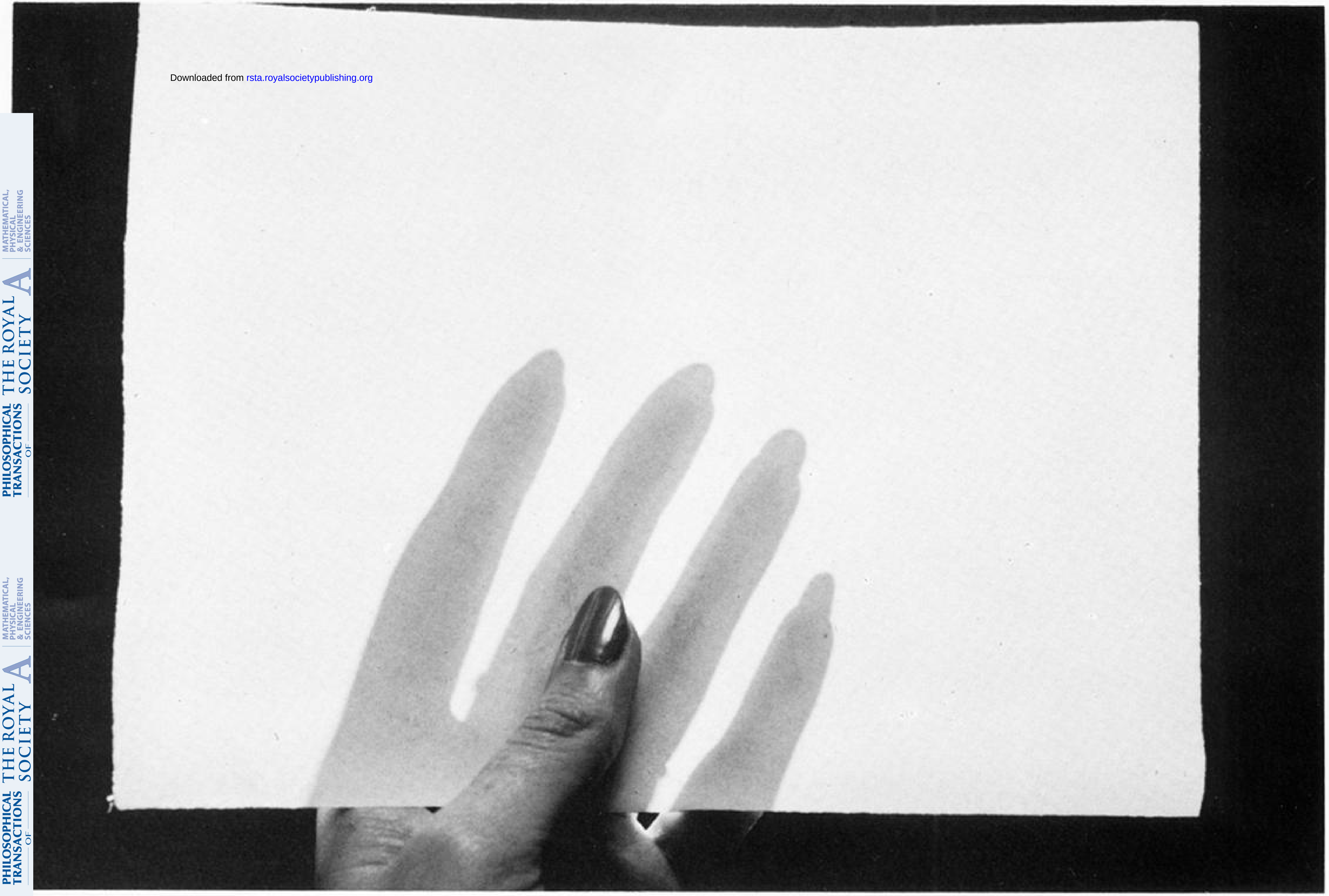

FIGURE 4. Sheet of NIMS cement: thickness 250 μm.