(12) UK Patent Application (19) GB (11) 2 168 693 A

(43) Application published 25 Jun 1986

(21) Application No **8431742**

(22) Date of filing **15 Dec 1984**

(71) Applicant
T&N Materials Research Limited (United Kingdom),
20 St Mary's Parsonage, Manchester M3 2NL

(72) Inventors
Alan William Atkinson
Anthony Thomas Walsh

(74) Agent and/or Address for Service
D D E Newman, R F Hadfield, J A Crux,
PO Box 20, Ashburton Road West, Trafford Park,
Manchester M17 1RA

(51) INT CL^4
C04B 38/06 26/04

(52) Domestic classification (Edition H):
C1H 120 517 610 748 762 813
U1S 1700 C1H

(56) Documents cited
GB 1212195 **EP A1 0055035**

(58) Field of search
C1H
Selected US specifications from IPC sub-class C04B

(54) Treatment of cementitious products

(57) Shaped products (e.g. sheets) comprising a matrix of water-insolubilised organic polymeric material (such as hydrolysed vinyl acetate polymer) filled with set hydraulic cement, as described for example in European Patent Publication 55 035 (ICI), have an unusually high flexural strength, above 40 MPa, but this falls considerably when the products are heated above about 250°C. By the invention, the extent to which flexural strength of such products is lost when they are heated is reduced, by first heating to burn out the organic polymeric material, and then bringing the product into contact with water to form a set cement in the interstices left by the burnt-out material.

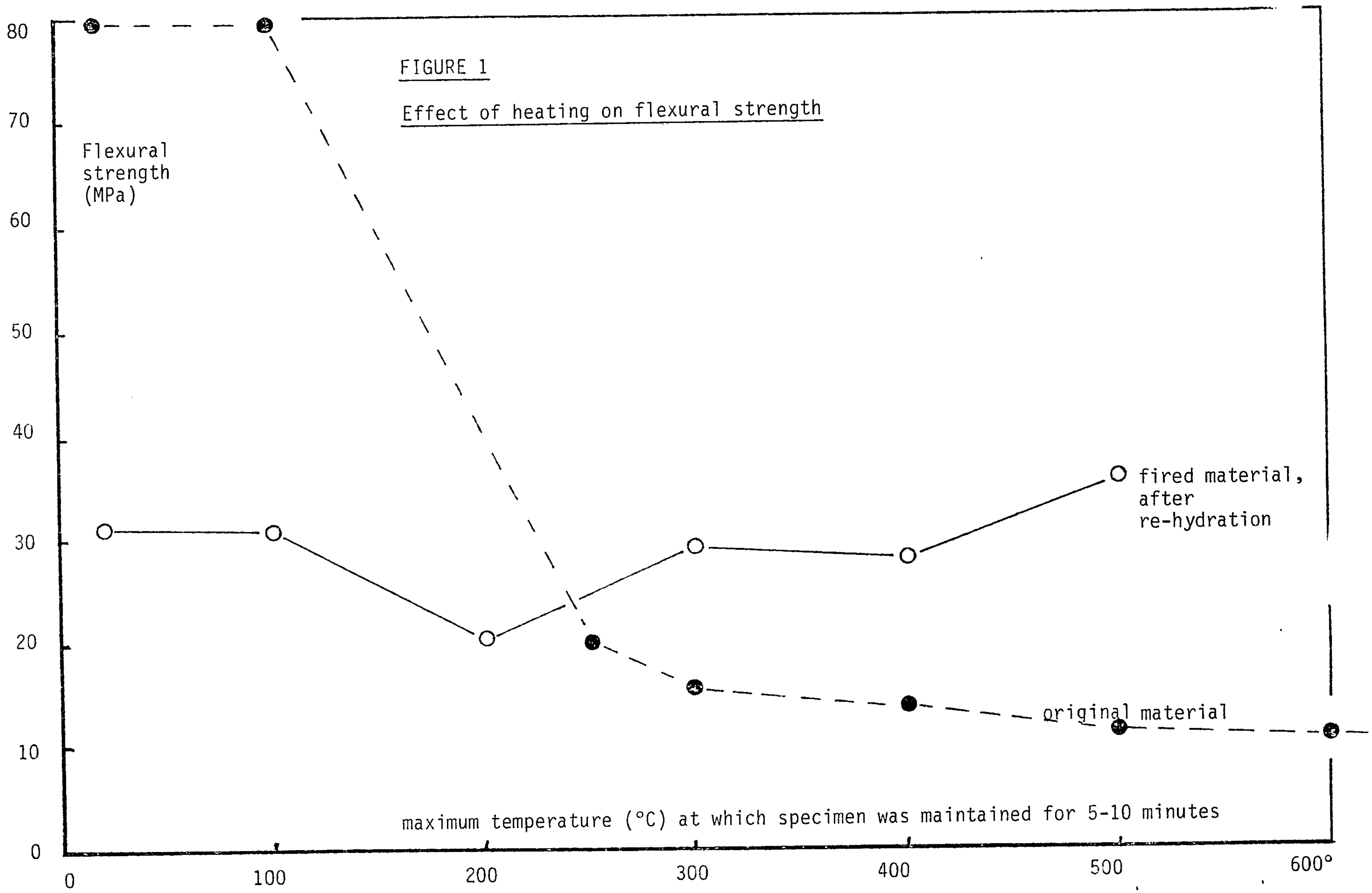
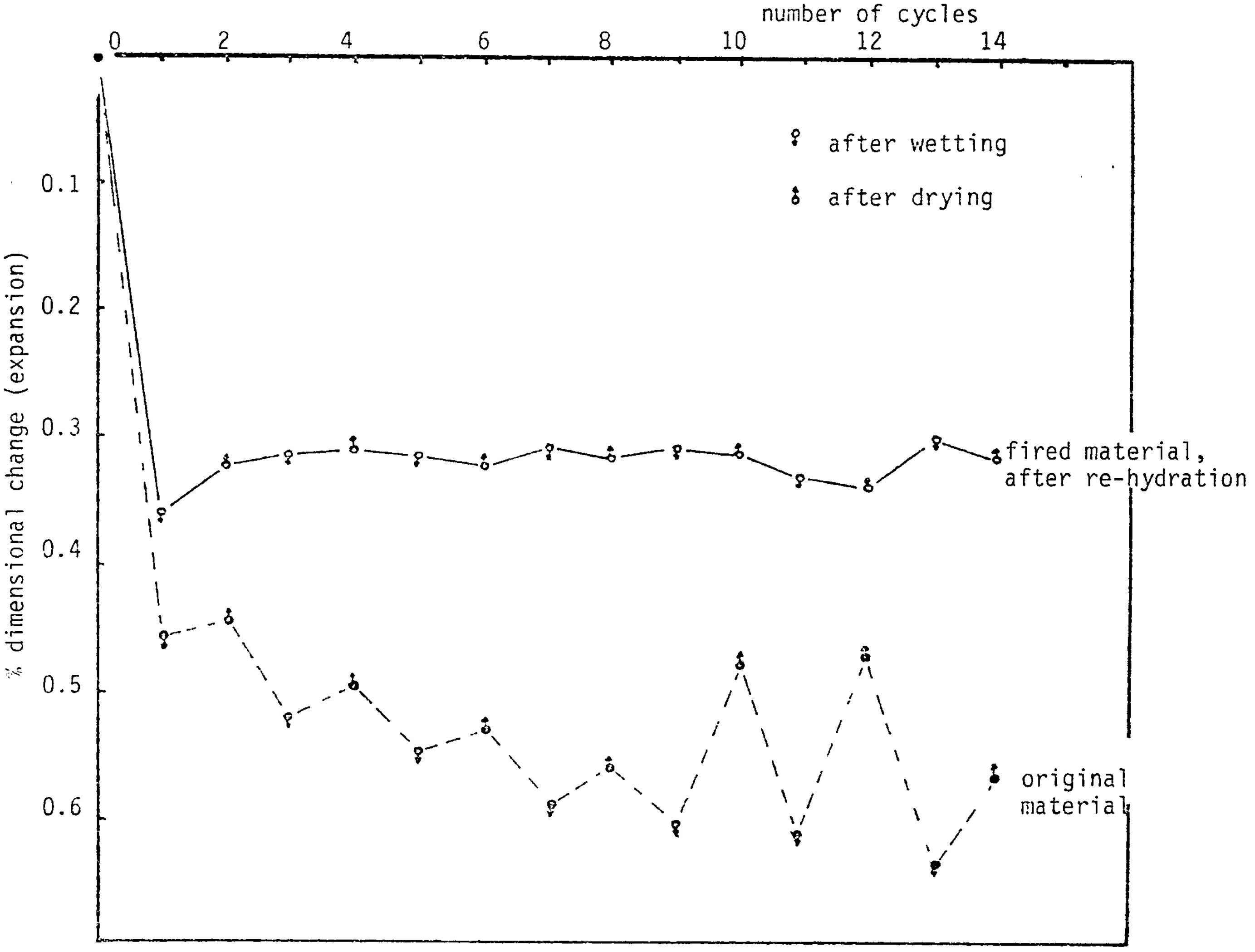


FIGURE 1

Effect of heating on flexural strength

FIGURE 2

Effect of Wet/Dry Cycling on Dimensions (Moisture-Movement)



SPECIFICATION

Shaped cementitious products

This invention relates to shaped cementitious products.

In European Patent Publication 55035 of Imperial Chemical Industries Plc there are described shaped cementitious products of flexural strength above 40MPa produced by the setting of a cementitious composition comprising hydraulic cement, water in an amount not more than 25% by weight of the composition, and a water-soluble or -dispersible organic polymer or copolymer in an amount of 1 to 15% by weight of the hydraulic cement. The cement and the organic polymeric material are selected so that a test composition comprising 100 parts by weight of cement, 5 parts by weight of the organic polymeric material and 16 parts by weight of water when extruded in a capillary rheometer undergoes an increase of at least 25% in shear stress when a ten-fold increase in the shear rate of the test composition is effected when the shear rates as measured are within the range 0.1 to 5 second^{-1}.

The organic polymeric material, which serves as a processing aid during preparation of the cementitious composition by high-shear mixing, is preferably a hydrolysed vinyl acetate polymer or copolymer, particularly hydrolysed poly(vinyl acetate), the degree of hydrolysis being preferably at least 50%: ie 50% of the vinyl acetate units in the polymer or copolymer are hydrolysed to the alcohol form.

The flexural strength of the shaped products is improved by ensuring that only a very small proportion, preferably not more than 2%, of the total volume of the set product, includes pores having a maximum dimension exceeding 100 microns as measured by quantitative microscopy, as described for example in an earlier European Patent Publication (21 682) of Imperial Chemical Industries Plc. The maintenance of high flexural strength in the shaped product is assisted by including a high-boiling polyol for example, glycerol, an alkylene glycol or a polyalkylene glycol, in the composition before setting.

In experimenting with the products just considered we have found that their flexural strength, although remarkably high, falls considerably when they are used at temperatures above about 250°C. For example, as illustrated later in this specification, a product of initial flexural strength 80 MPa may, on being heated to 300°C and kept at that temperature for 5 minutes, deteriorate to a strength of only about 15 MPa. This loss is permanent ie it is not regained on cooling.

The present invention is concerned with reducing the extent to which the flexural strength of such products, and others like them, is lost when they are subjected to high temperatures.

In arriving at the invention, we have to some extent been helped by recasting the terms in which we have thought about the products concerned. We have now come to regard them as essentially comprising a matrix of water-insolubilised organic polymeric material filled with set hydraulic cement, rather than as a matrix of set hydraulic cement in which the organic polymeric material that is present contributes little once it has served its purpose during processing. The organic polymeric material employed in making the cementitious composition loses its water-solubility or -dispersibility as a result of the action upon it of the water-soluble metallic compounds that are present in the hydraulic cement or are released from the cement during setting. However, even in that insolubilised state the organic polymeric material will not be immune to destruction when the product is subjected to a temperature above about 250°C; and when that happens, the framework of the product will be burnt out and so the strength of the product will be drastically reduced.

It has occurred to us that the way to deal with the problem is to put into the interstices left by the vanished 'organic' framework something that is much more resistant to elevated temperature.

According to the invention, we heat the shaped product to burn out the organic polymeric material; and subsequently we bring the product into contact with water to form a set cement in the interstices left by the burnt-out material.

Conveniently, the contact with water is brought about by simple immersion in water.

To burn out the organic polymeric material from the shaped product of high flexural strength it is convenient to proceed by raising the temperature from ambient to 400°C, and keeping it at that value for 30 minutes. Less time will be needed if a higher temperature, eg 500°C, is used.

The invention is further illustrated by the following Example:

Example

Following generally Example 1 in Imperial Chemical Industries Plc European Patent publication 55 035, a mixture was prepared of the following ingredients:

	Parts by weight
Cement Fondu Lafarge (a calcium aluminate cement of 40% Al_2O_3 content)	100
Hydrolysed poly(vinyl acetate) (GOHSENOL KH 17S; about 80% hydrolysed)	7
Glycerol	0.7
Water	11.5

The ingredients were first blended in a planetary mixer to a damp-crumb consistency. The material was then transferred to a twin-roll mill, and within 1 minute had become formed into a sheet with the consistency of a rubbery dough.

The sheet was removed and stored at ambient temperature and 100% relative humidity for seven days, to allow hydration of the cement.

Once hardened, the cement sheet was cut into 100 mm×15 mm×3 mm specimens suitable for flexural strength testing. Some of the specimens were allowed to air-dry, and others were fired at 400°C in air for 30 minutes to burn out the water-insolubilised hydrolysed poly(vinyl acetate). The fired specimens were then immersed in water (at 20°C) for 7 days to rehydrate them (ie to form set cement in the interstices of the product), air dried, and tested for flexural strength. Strengths were measured by 3-point bending.

The results of the strength tests were:

	Flexural Strength MPa
Air-dried specimens	74
Fired specimens	8
Fired specimens, after rehydration	30

The rehydrated fired specimens were then heated to temperatures in the range 100–600°C. Each specimen was kept at its maximum temperature for period of 5–10 minutes, then allowed to cool to room temperature. When cool, its flexural strength was measured. The results are shown in Fig. 1, which also shows the flexural strengths of some original specimens (ie specimens not previously fired, and not rehydrated) which had been (a) heated to the indicated maximum temperature (b) kept at that temperature for 5–10 minutes (c) cooled to room temperature.

It is clear that, at temperatures above 300°C, the rehydrated fired specimens keep their strength at a level of about 30 MPa, whereas the original specimens retain a strength of only about half that value or less.

Another benefit resulting from firing followed by rehydration was the improved retention of useful properties on prolonged contact with water. First, the surface material did not lose its hardness; and secondly, its expansion ('moisture movement') was considerably reduced. Fig. 2 shows the change in dimensions brought about by alternately wetting and drying, and it is clear that the rehydrated fired material suffers less expansion than the original material on initial wetting, and subsequently shows much less expansion and contraction on wet/dry cycling. This improved stability has promise for utility in the manufacture of building products to be exposed to the weather.

CLAIMS

1. A method of treating a shaped cementitious product comprising a matrix of water-insolubilised organic polymeric material filled with set hydraulic cement to reduce the extent to which flexural strength decreases above 250°C, in which the shaped product is heated to burn out the organic polymeric material, the product being subsequently brought into contact with water to form a set cement in the interstices left by the burnt-out material.
2. A method according to claim 1, in which the hydraulic cement is an aluminous cement.
3. A method according to claim 1 or 2, in which the organic polymeric material is a hydrolysed vinyl acetate polymer or copolymer.
4. A method according to claim 1, substantially as illustrated with reference to the Example herein.

Printed in the United Kingdom for Her Majesty's Stationery Office, Dd 8818935, 1986, 4235.
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.