JOURNAL OF MATERIALS SCIENCE 26 (1991) 1199–1204

Environmental degradation of macrodefect-free cements

Part I *Mechanical properties investigation*

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The effect of different environments on the flexural strength of a range of macrodefect-free (MDFs) cements was studied. The results showed significant differences in behaviour of the MDFs. These differences were found to be clearly related to the cement system the MDF was made from.

Initial measurements clearly established that high alumina cement (HAC) based MDFs were significantly stronger than ordinary Portland cement (OPC) based ones.

Upon immersion in water the flexural strengths were observed to drop initially. In the OPC MDFs some recovery in strength was subsequently observed. No such behaviour was found in the HAC MDFs. One of the MDFs studied had had the polymer removed prior to testing. This showed no sign of loss of strength on immersion in water but this could be due to the processing rate used to prepare it.

Gamma irradiation was more damaging to HAC MDFs than OPC MDFs. Gas analysis suggested that polymer degradation was occurring and it is proposed that the polymer matrix in HAC MDFs may be responsible to a degree for the high strength of these materials.

1. Introduction

Macrodefect-free (MDF) cements derive their name from the absence of the large scale (> 200 μm) porosity normally found in cement. This is achieved by a processing route which has a low water to cement ratio, a polymeric processing aid and high shear mixing [1–3]. The resulting material shows a considerable increase in flexural strength compared to the same cement produced by conventional techniques. In high alumina cement (HAC) MDFs the flexural strength is ~200 MPa compared to 20–30 MPa for a normal HAC.

Theoretically any hydraulic cement can be used to make a MDF. In practice it is found that some cements are very sensitive to the polymeric agent and before the MDF can be produced a suitable polymer needs to be found. For example, high alumina cement produces MDF with polyvinyl alcohol–acetate (PVA), and an ordinary portland cement (OPC) MDF with PVA or hydroxy propyl methyl cellulose (HPMC) or polyacrylamide as the polymeric aid.

Two alternative theories exist which attempt to explain the reasons for the high strength of the MDF. The first is that the reduction in pore size is responsible [4]. The second is that some form of chemical reaction occurs between the cement and the polymer [5]. Whilst the exact cause of the enhanced strength is subject to debate it is clear that the MDFs represent a considerable advance in the search for high strength cements.

Recently it has been established that MDFs are altered by exposure to different environmental conditions [6–9]. Three conditions have been identified as showing deleterious effects on some MDFs: heat, gamma irradiation and immersion in water. This paper explores these effects. In particular it looks at whether the polymer and cement used to make the MDF play any significant role in determining the response of the material to their environment. Where possible some explanation of the observed changes will be offered but these arguments are explored in more detail in a second paper which looks at changes in the microstructure and chemistry of the MDFs in an attempt to understand the mechanisms which are responsible for alterations in properties.

2. Experimental procedure

2.1. Materials

A range of MDF materials were supplied by ICI. Their compositions are shown in Table I. The material was supplied in the form of thin sheets which were cut to produce beams ~5 mm × 50 mm × sheet thickness.

2.2. Sample conditioning

Following Pearson's work [6] three different environmental conditions were studied: water immersion, gamma irradiation and heating at 110 °C. If sufficient material was available the range of conditions shown in Table II were studied otherwise a more limited

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TABLE I Materials studies

1. NIM 127 HAC PVA based
2. NIM 125 HAC PVA based
3. NIM 223 – with a heat treatment to remove the polymeric phase
4. OPC based MDF based on HPMC
    - 4i 7 day cured*
    - 4ii 14 day cured
    - 4iii 28 day cured
5. OPC based MDF with PVAL
    - 5i 7 day cured
    - 5ii 14 day cured
    - 5iii 28 day cured

*Material was allowed to hydrate for *x* days then dried to stop any further hydration

TABLE II Test schedule (optimum)

Water immersion	Temperature (°C)	Treatment
3 h u/w	20	a
	50	a
	20	b
	50	b
24 h u/w	20	b
	50	b
	20	b
	50	b
7 days u/w	20	b
	50	b
	20	b
	50	b
14 days u/w	20	b
	50	b
	20	b
	50	b
28 days u/w	20	b
	50	b
	20	b
	50	b
57 days u/w	20	b
	50	b
	20	b
	50	b
As-received		
Heat – 110 °C for 2 h		
Gamma Irradiation	300 MRad and Test – with control	
	600 MRad and Test – with control	
	900 MRad and Test – with control	

a tested u/w
b air dried 24 h then tested "dry"

range was investigated. Samples for water immersion were placed in a water bath at 20 or 50 °C until the requisite time and then tested under water or after drying for 24 h in air.

Gamma irradiation was carried out by placing samples in sealed stainless steel tubes into the Harwell spent fuel storage facility. The samples were irradiated at a dose rate of 10^4 Gy h^{-1} in dose intervals of 3 MGy. As a result of radiation heating at this dose rate, samples reached an equilibrium temperature of ~50 to 52 °C during irradiation. Consequently, control samples were maintained at this temperature to ensure that any changes in strength were due to gamma irradiation and not thermal degradation. The effect of dose rates was not investigated. One problem encountered with this work was the failure of valves used to seal the samples. If this occurred then no mechanical properties were measured as the ingress of water represented an additional factor which was not possible to allow for. There was insufficient material available to repeat any work if the tube failed.

Samples for heat exposure tests were placed in an oven at 110 °C for times of up to 2 h and then cooled and tested.

2.3. Strength testing

Flexural strength was measured in a three-point bend test on an Instron universal test machine using a 34 mm span and 5 mm min^{-1} crosshead speed. Untreated samples of each material were tested to establish base line data. The strengths quoted are the average from five or ten samples as this represents the minimum number of samples required to give a value free from major statistic variations due to variability of the material.

3. Results and discussion

3.1. As-received mechanical properties

The average flexural strength of each material prior to any environmental exposure is shown in Table III.

3.2. Water immersion

Pearson [6] and more recently Cannon [7] and Poon [8] at Oxford have all shown that a HAC-based MDF is degraded by immersion in water. The majority of this work was carried out on a single material, NIM 127, provided by ICI. In this current work a wider range of HAC-based MDF was tested. The results of the tests are shown in Fig. 1 and Table IV.

Fig. 1 confirms the results of the previous authors and shows that NIM 127 is degraded very quickly on

TABLE III As-received strength

NIM 127	168 MPa
NIM 127 HT	168 MPa
NIM 125	160 MPa
NIM 223	54 MPa
OPC PVAL 7 day	47 MPa
OPC PVAL 14 day	54 MPa
OPC PVAL 28 day	46 MPa
OPC HPMC	29 MPa
OPC HPMC 28 day	44 MPa

TABLE IV Affect of water immersion on flexural strength of NIM 125 and NIM 223

Condition	σ(MPa)	
	NIM 125	NIM 223
As-received	160	55
48 h in water 20 °C	103	56

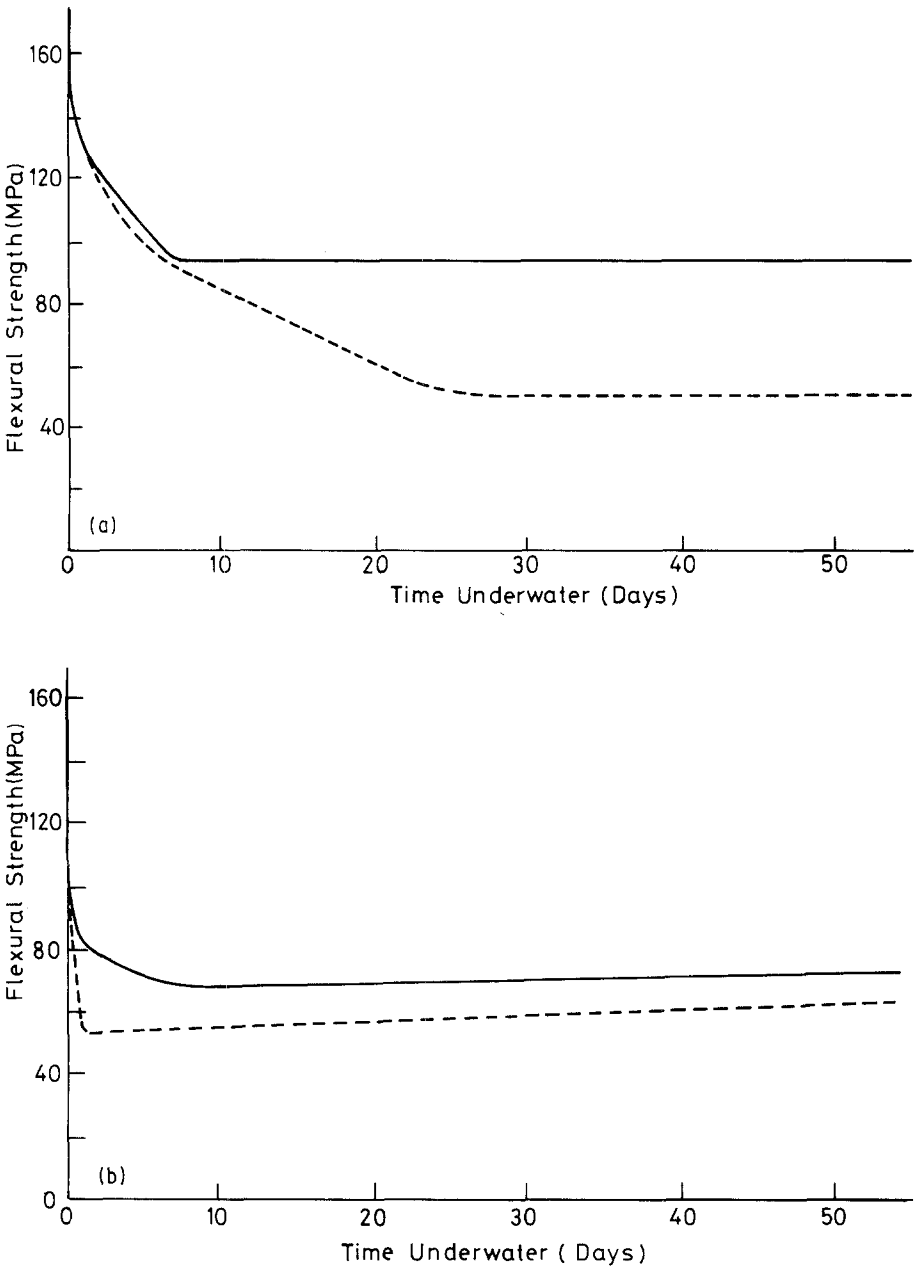

Figure 1 Effect of water immersion on flexural strength of (a) NIM 127 at 20 °C and (b) NIM 127 at 50 °C (——tested wet, --- tested dried).

immersion in water. More strength is lost by drying the samples, in air, at room temperature for 24 h prior to testing. This is presumably due to some form of shrinkage cracking which occurs on drying. This is in contrast to the data in Poon's paper but the effect is genuine and reproducible at 20 and 50 °C.

NIM 125 is a similar MDF to NIM 127 with a slightly lower polymer content. Unfortunately very few samples were available and it has only been possible to show that the strength drops in a similar way for both materials.

NIM 223 is an unusual material in that the polymer has been removed by heating to 500 °C to burn out the polymer and the material rehydrated to partially restore the strength. This is the only HAC-based MDF which does not undergo a catastrophic reduction in strength on immersion in water. This could of course be due to the fact that it has already undergone the reduction in strength process during its rehydration operation, or it may be that the polymer is responsible for the strength in the HAC MDF and this is susceptible to attack by the water. These aspects will be explored in more detail in a companion paper which looks at microstructural and chemical changes occurring as a result of environmental exposure.

The HPMC OPC MDF are also degraded by the action of water, Figs 2 and 3. It is not known why the 14 day old sample of HPMC–OPC MDF was weaker than the 7 and 28 day materials but all three materials behaved in a similar way. The material is initially degraded by exposure to water but it appears to undergo a strengthening process with further exposure. There is some suggestion that at 50 °C after 7 days a peak strength is achieved with a gradual decline in strength over the next 21 days. At 20 °C there is more evidence to suggest that the strength continually rises but this may be due to any subsequent deleterious reaction with water taking longer and hence lying outside of the timescale of the experiment. Very much the same trend is observed in the OPC PVAC MDF with an initial drop in strength on immersion and a subsequent recovery of strength.

It is very interesting to compare OPC PVAL MDF with NIM 127 which contains the same polymer system (Figs 1 and 3). Both the OPC and HAC MDFs show a similar drop in strength over the first 24 h

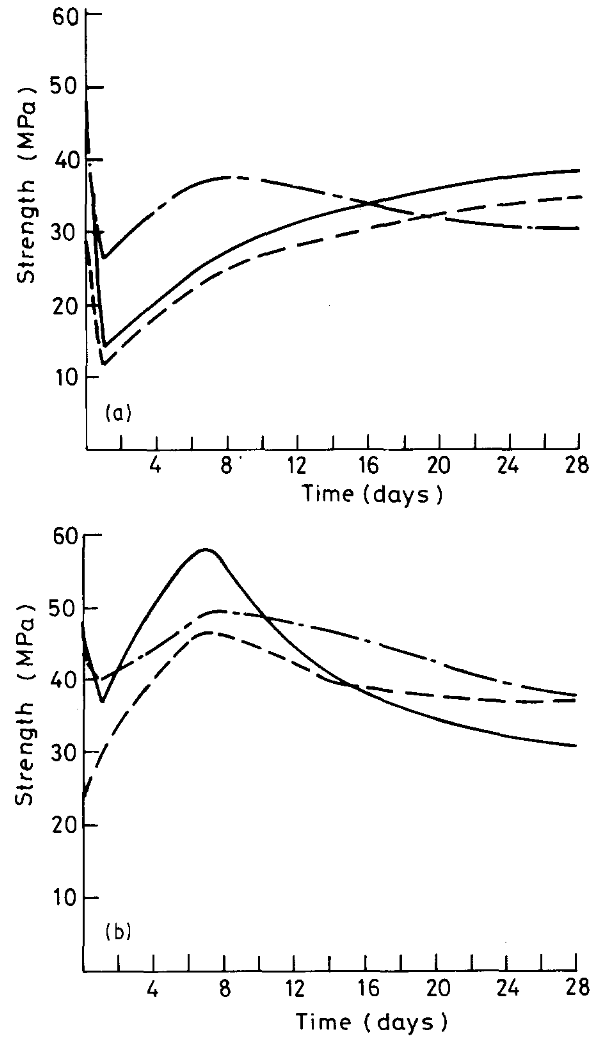

Figure 2 Effect of water immersion at (a) 20 °C on strength of HPMC–OPC MDF and (b) 50 °C (—— 7 day initial cure, --- 14 day initial cure, —·— 28 day cure).

immersion period. Thereafter the behaviours diverge with the HAC continuing to lose strength over the next 7 days (at 20 °C). At 50 °C the HAC drops more dramatically in strength and after 24 h there is little evidence of any further strength loss with continued immersion. This suggests that a significant difference exists between the OPC and HAC systems. Recent work has shown that HAC based MDF are not hydrating in the normal way and it has been suggested [10–12] that the polymer may be responsible for binding the material together. Since the polymer is susceptible to water ingress, any exposure to water would result in a drop in strength. The difference between the HAC and OPC systems could lie in the nature of any subsequent hydration product.

3.3. Gamma irradiation

The results of the gamma irradiation experiments are shown in Fig. 4 and Table V. It is clear that the drop in strength in the HAC MDFs is due to the gamma irradiation as the controls show no appreciable change. Gas analysis, see Table VI, shows that there are two effects occurring. In the gamma flux oxygen is absorbed and hydrogen and CH_4 are released. The controls also show a similar amount of oxygen

TABLE V Flexural strength gamma irradiation and controls

	300 MGy	Control	600 MGy	Control	900 MGy	Control
NIM 127 (MT)	31	155	42	127	31	—
NIM 125	64	136	52	122	35	—
OPC PVAL						
7 days	36	—	31	—	36	—
14 days	39	—	36	—	30	—
28 days	—	—	—	—	—	—
OPC HPMC						
14 days	14	26	15	30	14	—

TABLE VI Gas analysis data—typical composition for NIM 127

gamma-irradiated				
3.8% H_2	1.2% O_2	93% N_2	1.3% CH_4	0.04% CO_2
control				
	1.26% O_2	97% N_2	1.74% CO	

Note: The gas analysis is similar for OPC and HAC MDFs

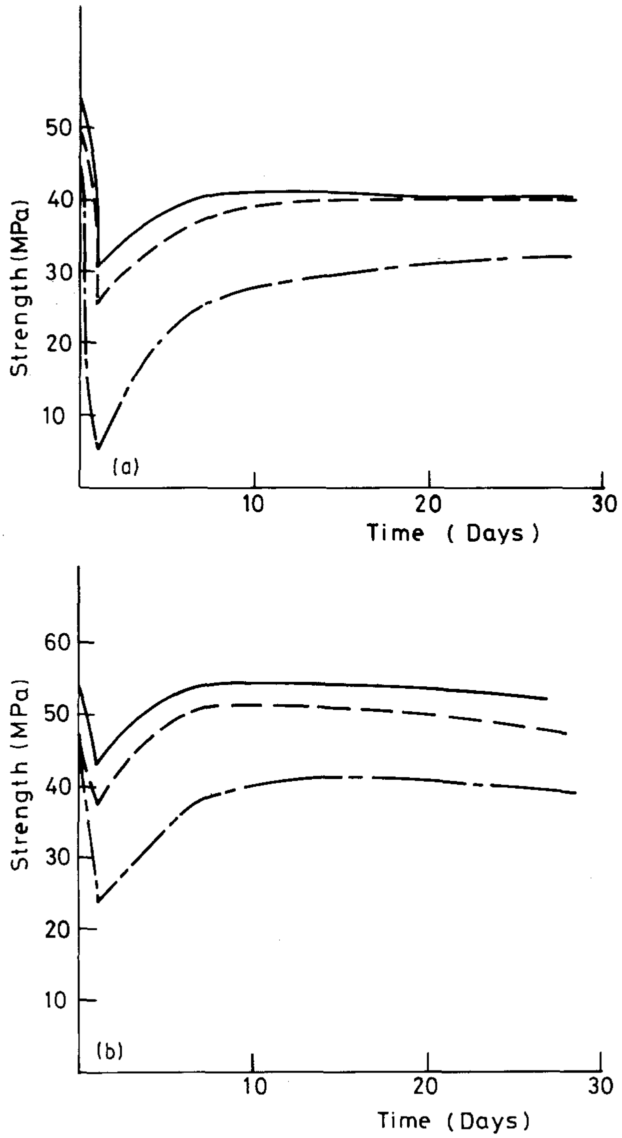

Figure 3 Effect of water immersion at (a) 20 °C and (b) 50 °C on flexural strength of PVAL–OPC MDF (—— 7 day, --- 14 day, — — — 28 day).

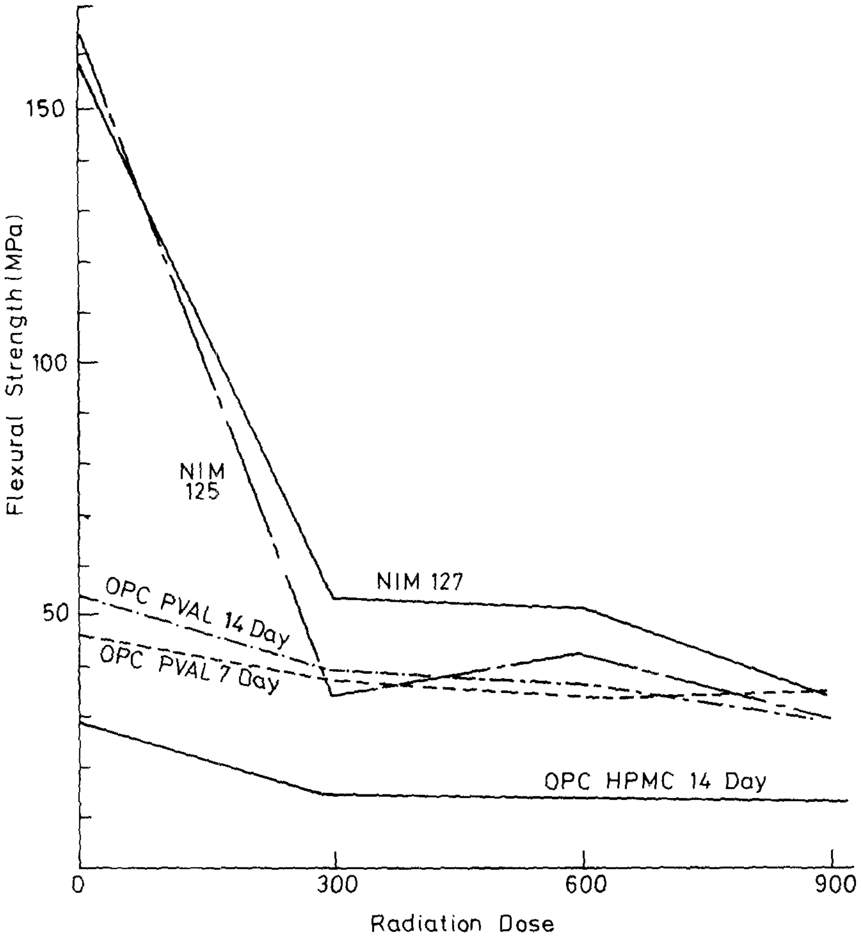

Figure 4 Effect of gamma-irradiation on flexural strength.

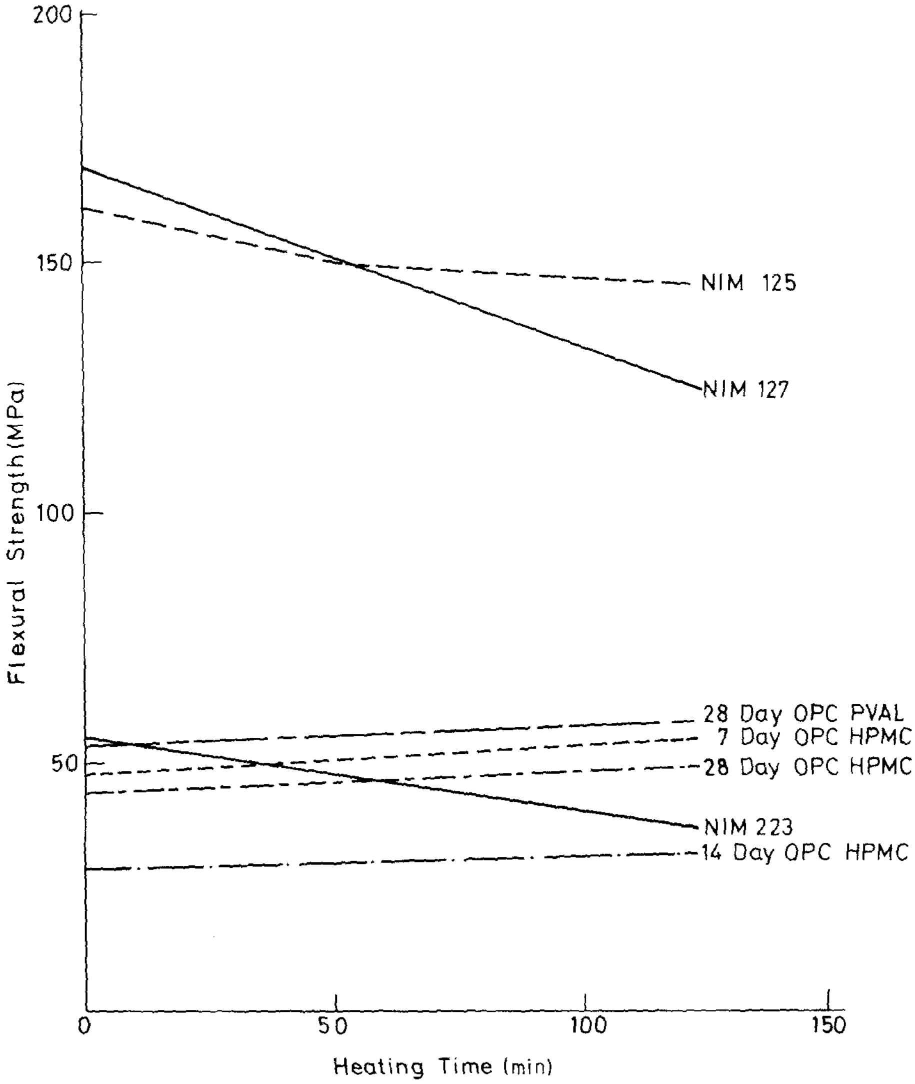

Figure 5 Effect of heat on flexural strength.

absorption but there is no hydrogen and CH_4 release. The most obvious source of CH_4 is from radiolysis of the polymer. The source of hydrogen is less clear. In normal cements subject to gamma irradiation hydrogen is produced by radiolysis of free water. In MDFs with their low w/c ratio there is not expected to be much free water. It is more likely that the production of hydrogen is associated with the polymer. Since the strength of the HAC MDF drops when radiolized it may be assumed that there is some link between the strength drop and the evolution of the gas. Polyvinyl alcohol is known to be degraded when subjected to gamma irradiation in a dry state [13] with a loss of tensile strength. Clearly a similar affect is occurring in the MDF.

The OPC-based MDFs show a much smaller change in strength as a result of gamma irradiation. Like the HAC MDF the gas analysis show the absorption of oxygen in both the gamma flux and the control. Similarly hydrogen and CH_4 are released only in the gamma irradiation.

Gamma irradiation studies on OPC-based cement systems [14] have shown that the oxygen absorption mechanism is complex. Three mechanisms have been suggested: surface adsorption, oxidation of reduced species and peroxy gel stabilization: all or some may be operative. In MDFs the polymer may also react with oxygen. It is probable that the hydrogen production is due to the polymer degradation rather than radiolysis of water as the low w/c ratio means that little if any free water would be expected in the MDF.

The difference between the behaviour of the OPC and HAC MDFs subject to irradiation is interesting. The strength of non MDF cements is not affected very much by gamma irradiation as is the OPC MDF system. It therefore appears that the HAC MDF is adversely affected presumably because the polymer matrix is in some way responsible for the bonding in this system.

3.4. Affect of heating at 110 °C

Fig. 5 shows the effect of heat on the average flexural strength of a range of MDF Materials. It is apparent that the HAC MDFs are more severely affected by the heat than the OPC-based MDFs. Without microstructural evidence it is difficult to account for this process. The behaviour will be discussed in more detail in the second paper.

4. Conclusions

The conclusions are as follows.

(1) HAC MDFs (with polymer present) are significantly stronger than OPC MDFs.

(2) HAC MDFs and OPC MDFs are degraded by immersion in water. The HAC system shows no sign of any recovery of strength with prolonged exposure whereas the OPC system does.

(3) The difference in behaviour of HAC and OPC MDFs in water is a function of the cement since one of the OPC MDFs uses the same polymer.

(4) The initial drop in strength of MDFs in water is common to all except the NIM 223 which has no polymer present suggesting that the polymer phase may be responsible for the behaviour.

(5) Gamma irradiation is more damaging to the HAC based MDFs. Since the gas analysis show that the polymer is degraded in OPC and HAC systems it may be that the polymer is responsible for a greater degree of binding in the HAC system.

(6) Heating reduces the strength of HAC MDFs.

(7) The properties of the MDF depend upon the cement system and the polymer system.

Acknowledgements

Thanks go to Andy Briggs, Dianna Nunn and David Ransom for their help with testing samples. This work forms part of the UKAEA underlying fracture programme. The paper is published by permission of Her Majesty's Stationery Office © Crown Copyright.

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Received 9 June
and accepted 23 October 1989