

## **INVESTIGATIONS INTO THE ROLE OF ACTIVATED CARBON IN A MOISTURE-BLOCKING CEMENT FORMULATION**

*B. Chowdhury*\*

Matech Associates, 407 WLE, Lake Ariel, PA 18436, USA

### **Abstract**

Physical deterioration is a natural consequence of moisture attack in finished concrete. Moisture is retained in open voids in prepared cement during mixing and hydration stages. Further atmospheric moisture uptake occurs following dehydration under use conditions in polymer-containing cement formulations, since polymers act as conduits for moisture ingress. The initial attribute of added strength from the polymer in improved cement formulations is thus nullified. Customary solution to the moisture problem has centered around improving moisture resistance by significant reduction of inherent macro defects. A more complete method of moisture blocking by the reaction of activated carbon with a vinyl polymer included in the cement formulation is described here. The moisture blocking action is due to the mitigation of open voids by the occlusion of a carbon–vinyl additive, essentially resulting in filled voids or no voids in the prepared cement, producing a durable finished concrete product.

Supporting evidence for the above by thermal, polarization, X-ray and SEM are reported in this paper.

**Keywords:** activated carbon, carbon–vinyl reaction, cement microstructure, moisture blocking, moisture in cement, polarizability, X-ray diffraction

### **Introduction**

This paper reports a simple and practical solution to the well-known problem of moisture attack in finished concrete and is based on a US utility patent awarded to the author. In particular, the paper describes a method of eliminating voids in finished products by the addition of activated carbon which results in a hydrophobic cement composition.

Moisture retention due to void formation typically during mixing of cement products and further moisture uptake following dehydration in cement applications result in localized failure points in solid concrete. Loss of structural integrity often leads to crack propagation and structural failure. Traditional cement technology has thus suffered from inadequate strength and durability of finished concrete. The

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\* Author for correspondence: E-mail: [matech@usnetway.com](mailto:matech@usnetway.com)

so-called Macro-Defect-Free (MDF) formulations [1–4] in the form of organo-cement composites have attempted to address these issues with limited success in reducing the critical population of open voids. Further improvement in moisture resistance is predicated on the elimination of open voids altogether.

Initial and subsequent MDF formulations contain one or more types of polymeric entities. Whereas the polymer content has been found to impart mechanical strength to the cement in terms of load bearing capacity, it also promotes detrimental moisture ingress [5–8]. Consequently, underlying research has aimed at increasing moisture resistance through changes in formulation and variations in the preparation procedure as a remedy [9, 10]. The polymer is required for strength in MDF formulations, but it also acts as a conduit for moisture uptake. The solution is based on rendering the polymer hydrophobic by the use of activated carbon in an MDF cement formulation comprising ordinary portland cement (mixture of calcium, iron and alumino-silicates), silica and a vinyl polymer. Incorporation of activated carbon in the cement mix completely eliminates the moisture retention and moisture uptake problems by inclusion of a carbon vinyl reaction product in the voids, as evidenced below.

## Experimental

### *Sample preparation*

Particular methods of sample preparation and testing were required since extraneous water in wet cement, as prepared, masks and prevents any distinguishing characterization.

Reference samples in the form of 6×0.75 cm discs were prepared by addition of plain water (C:W=7:1) to the cement mix and stirred to a loose paste consistency. The mixture was allowed to stand for 10 min and mixed again before casting the now stiff paste into the test discs. The prepared discs were heat treated in a 50°C convection oven for 24 h and then desiccated at an equilibrium moisture of 10% RH for another 24 h before exposing them to the laboratory atmosphere of 50% RH and 73°F before testing. Stored samples for later testing were conditioned at 50°C for 30 min prior to testing.

Carbonated samples were prepared in the same essential manner as above with the addition of 10, 25 and 50% of powdered activated carbon to the initial mass of cement mix. A gradual color change during preparation and within a period thereafter from very dark to a light buff is indicative of chemical transformation in the sample which is energetically favored by the hydration exotherm during mixing. The complex thermogenic manifestations of hydration in cements have been well documented in recent studies [11–13].

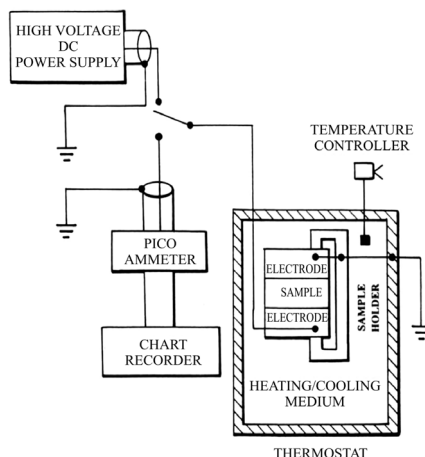
The activated carbon was produced by reductive burning of bio-organic waste materials for 30 min at 900°C under methane and a small excess of oxygen from air. EPR measurement has shown weak paramagnetism indicating presence of free valences in the ‘active’ carbon.

### *Thermal studies*

Standard DSC technique was used for the thermal studies.

### *Polarization*

The polarization technique for various materials has been described in the literature [14–16]. Carbonated sample specimens were individually subjected to 10 KV DC, which is just under the breakdown voltage of  $15 \text{ kV cm}^{-1}$ , at a heating rate of  $5^\circ\text{C min}^{-1}$  to a final temperature of  $205^\circ\text{C}$  and annealed for up to 60 min. The orientations of the charge domains due to polarization were ‘frozen-in-place’ by cooling the test materials back to ambient temperature under the voltage field over a period of time. An amount of current associated with these polarization orientations is thus preserved in the sample. Thermograms were obtained as depolarization current *vs.* temperature by heating the sample to beyond decomposition at  $5^\circ\text{C min}^{-1}$  without the voltage field. A schematic diagram for the polarization experiment is shown in Fig. 1.



**Fig. 1** Schematic of experimental SET-UP for polarization studies

### *X-ray diffraction (XRD)*

Although useful for examining cement composition, XRD is of limited value for studying component reactivity in cement formulations. Nevertheless, important information has been obtained by XRD (Philips diffractometer,  $\text{CuK}_\alpha$ -radiation, Ni-filter) analysis performed at the Slovak Academy of Sciences in Bratislava. Carbon and non-carbon cement samples were prepared by the addition of water (C:W=7:1) and only air-dried to examine the extent of initial hydration. Dried samples were desiccated for several days at  $<60^\circ\text{C}$  and were ground to particle sizes of less than 40 micron.

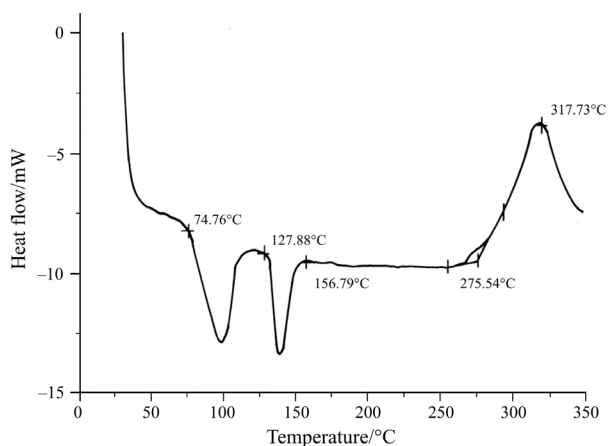
### *SEM and porosity*

Discs of cement and carbon–cement samples prepared in the manner described under ‘experimental’ were examined by SEM at the Slovak Technical University in Bratislava, using a Tesla BS 300 SEM with a TESCAN digital unit and a Balzers SCD/050 sputter coater. Accelerating voltage of 15 kV and various magnifications were used.

## Results and discussions

### *Thermal*

Figure 2 shows DSC endotherms due to loss of retained moisture in a prepared and conditioned untreated (non carbon) cement sample.



**Fig. 2** DSC curve of untreated cement

Evidence of further moisture uptake after exposure of a separate untreated cement sample to 100% RH in a closed environment for 48 h is shown in Fig. 3.

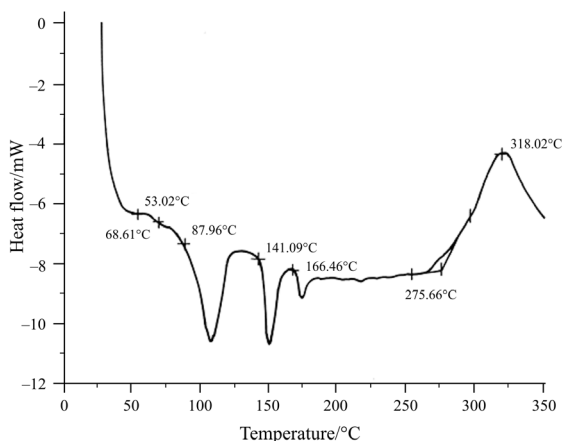
Figures 4 and 5 show total absence of moisture but appearance of the dry polymer  $T_g$  for the carbon–cement compositions of 10 and 25% carbon in cement is evident.

Figures 6 and 7 confirm that no moisture uptake occurs in 25 and 50% carbon samples even after exposure to 100% RH.

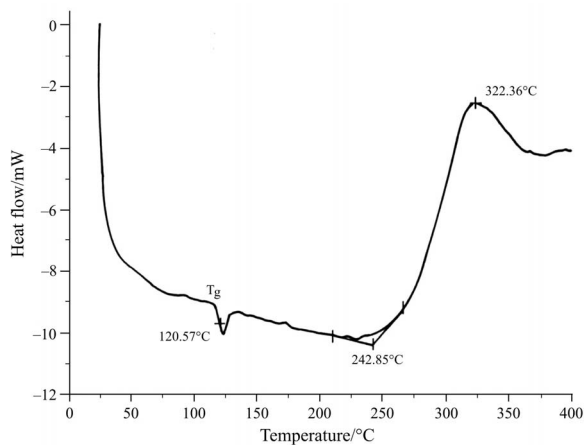
One evidence of the reactivity of carbon with the vinyl polymer is the stiffening of the polymer, since  $T_g$  value increases with increasing carbon content.

### *Polarization*

Figure 8 illustrates the depolarization thermograms and hence the polarizability of the carbon–cement composites. The  $T_g$  values are the same as obtained by DSC, followed by high temperature material decomposition.



**Fig. 3** DSC curve of untreated cement exposed to 100% RH



**Fig. 4** DSC curve of 100% carbon in cement

The wide (diffuse) dispersion of the polarization peaks indicate lack of ordered structure or crystallinity in the polarized material. Additionally, the linear distribution of relaxation times, shown in Fig. 9, calculated [17] from these depolarization currents indicate that a single dipolar species is present in the cement samples at all carbon levels. Multiple dipole activity would produce scattered data.

Cement or carbon on their own lack particular dipolar characteristics that can interact with an applied voltage field. Prepared non-carbon samples cannot be properly tested since they do not produce measurable electrode potential difference. The polarizability of carbon-cement samples must therefore arise from the reactivity of carbon to alter the specificity of the electroactive vinyl polymer to produce a carbon–vinyl adduct in the cement mix. It has been suggested [5] that the success of MDF cements in moisture resistance is due mainly to the component polymer acting

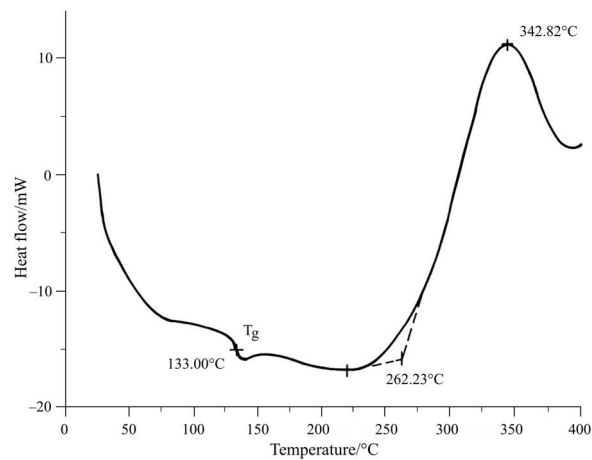


Fig. 5 DSC curve of 25% carbon in cement

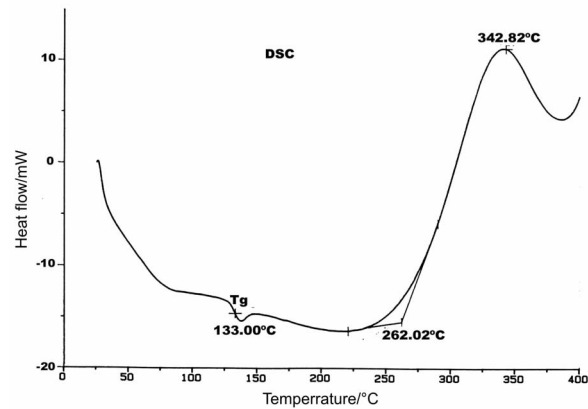


Fig. 6 DSC curve of 25% carbon cement exposed to 100% RH

as a filler in large voids. The filler in this case is the above-mentioned adduct and not the polymer alone. The conformation of a carbon–vinyl adduct can be realized by invoking an electron promotion mechanism from the ground state configuration of the active carbon:  $C(1s^1 2s^2 2p^2) \rightarrow C(1s^1 2s^1 2p_x^1 2p_y^1 2p_z^1)$ , providing valence shells for acceptance of labile  $\pi$ -electrons of the vinyl double bonds. High voltage polarizability stems from mutual polarization of induced dipoles in the adduct thus produced and not from an ordered structure.

#### *X-ray diffraction*

The aligned X-ray diagram of diffraction lines for carbon and non-carbon samples shown in Fig. 10 is primarily characterized by the absence of ettringite and ettringite-like hydration products between 5 and  $10^\circ\theta$ . XRD lines of silica are evi-

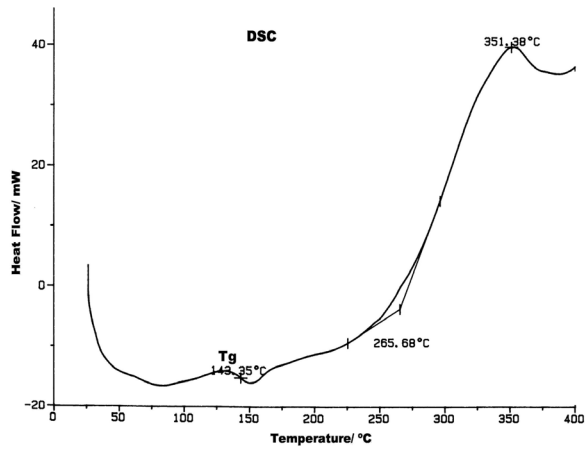


Fig. 7 DSC curve of 50% carbon in cement exposed to 100% RH

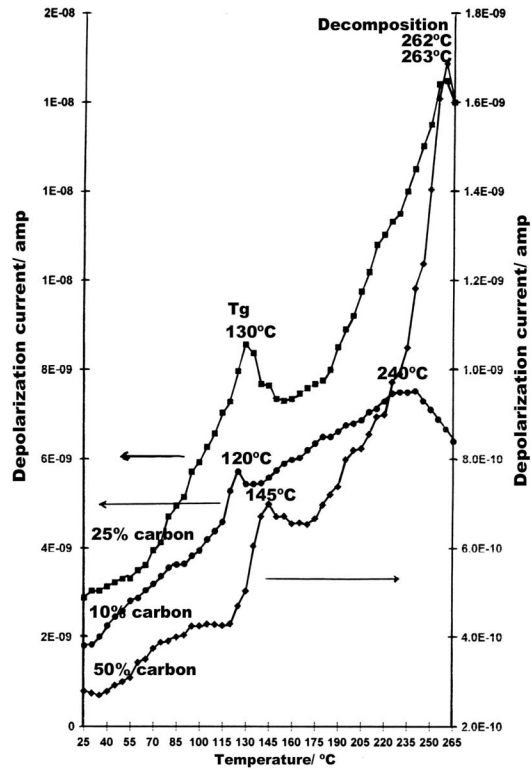


Fig. 8 Depolarization current vs. temperature

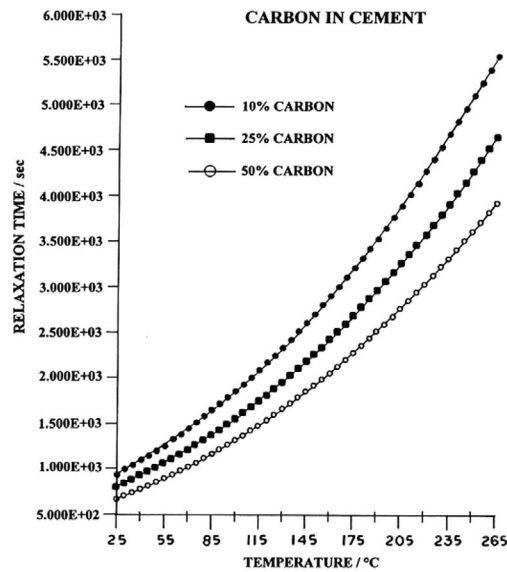


Fig. 9 Relaxation time vs. temperature

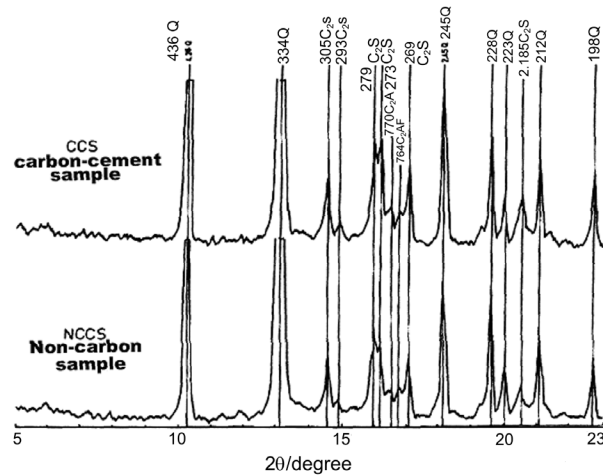


Fig. 10 X-ray diffraction lines for carbon and non-carbon samples

dent at 4.26, 3.34 and 2.45–1.98 Å. The doublet at 2.79–2.75 Å proves presence of unreacted cement minerals  $C_3S$  and  $C_2S$ . It is clear that carbon does not participate in any reaction with the cement minerals. Free or unreacted carbon is not expected to be present in view of its reaction with the vinyl polymer, but its presence cannot be confirmed. The carbon diffraction line at 3.35 Å is swamped by the predominant silica line at 3.34 Å.  $C_3S$  is confirmed by XRD lines at 3.06, 2.99, 2.615 and 2.185 Å. This



confirms significant amount of unreacted anhydrous calcium silicate mineral occurring in both carbon and non-carbon samples, eliminating the possibility of production of voluminous ettringite or nucleation and crystallization of  $\text{Ca}(\text{OH})_2$  particles. Main XRD lines of  $\text{Ca}(\text{OH})_2$  at 4.91 and 2.64 Å are missing. All these confirm low initial hydration. Unlike polarization, X-ray can not verify interaction of amorphous carbon with the filler polymer due to lack of crystallinity in the reaction product. Any crosslinks also can not be detected because X-ray is transparent to organic phase.

#### *SEM and porosity*

Several distinct differences were observed in the microstructure of the two types of samples under study. Large spherical pores or ‘macropores’ (about 0.5 mm/380–660 μm), appearing as black holes, can be seen clearly in the cement sample, shown in Fig. 11.

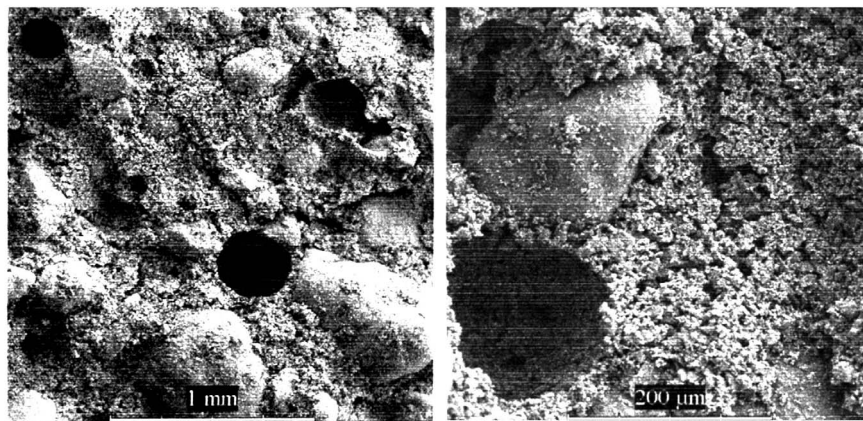


Fig. 11 Microstructure of cement sample

These pores are absent in the carbon-cement sample (Fig. 12) and filler material is evident. Plate particles are seen to cover longitudinal pores without any particular orientation as would be expected for the dispersion of the polymer network. The microstructure of activated carbon itself in SEM Fig. 13 appears as flat, large surface-area particles covered with moisture beads, confirming its hydrophobic nature so that any free carbon can also restrict cement–water exchange during the initial hydration stage.

Subsequent moisture uptake leading to Crack formation in non-carbon cement is associated with the breakage of the small linked particles of CSH gels, as seen in Fig. 14, whereas crack propagation is prevented in carbon-cement samples by slip-page along the plain surfaces of the carbon particles.

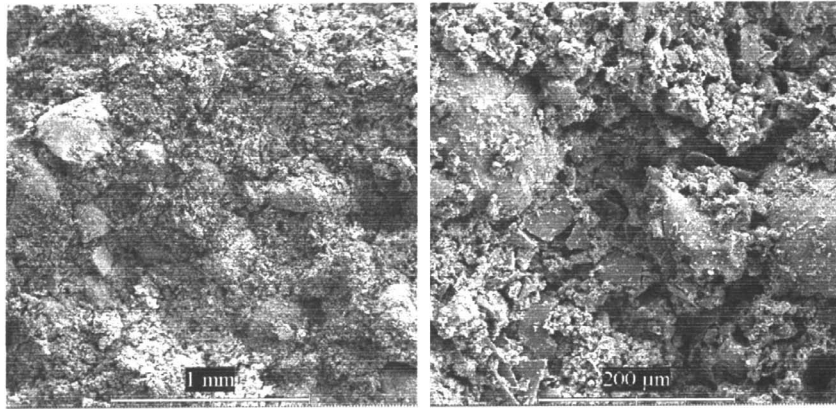


Fig. 12 Microstructure of carbon-cement sample

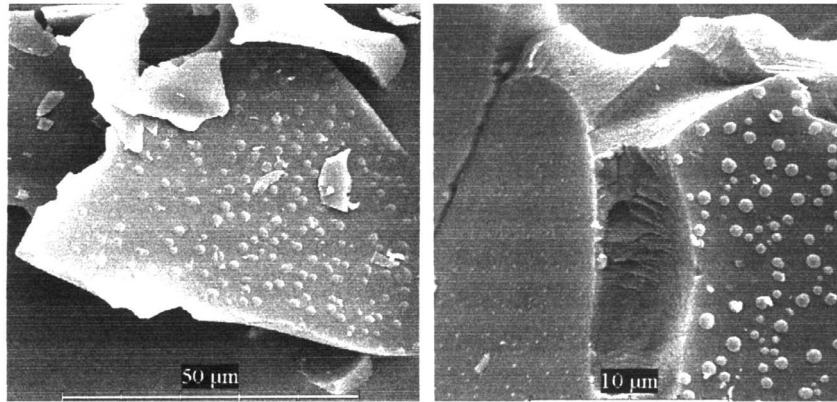


Fig. 13 Microstructure of activated carbon

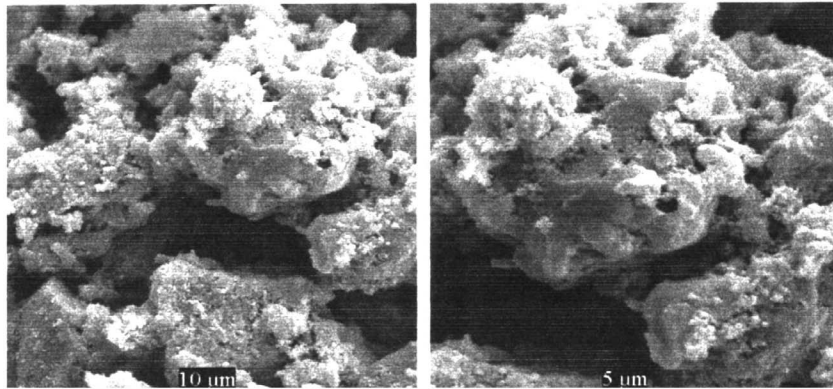


Fig. 14 Crack propagation in cement sample

## Conclusions

Widespread attempts at prevention of structural damage by retained moisture in the aggregate porosity of finished concrete have given rise to the use of polymers in the so-called Macro-Defect-Free (MDF) formulations that produce significantly reduced open voids. Polymers have added measurable strength to cement products but have also contributed to compromised moisture resistance in cement applications. Incorporation of activated carbon as an additive in an MDF cement formulation containing a vinyl polymer has been found to completely satisfy the aim of MDF cements for producing a moisture-blocking durable cement material. Comparative results by thermal analysis for carbon and non-carbon samples exposed to conditions of high humidity have verified total moisture resistance for carbonated samples. High voltage polarizability of only the carbonated samples signifies formation of a new entity in these samples that is absent in regular cement with the polymer alone. X-ray diffraction analysis has provided further evidence of low initial hydration which is a characteristic of MDF cements. SEM pictures have provided conclusive evidence of the moisture blocking ability of carbonated cement.

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