

Evaluation of Self-degradability of Sodium Carboxymethyl Cellulose (CMC) in Alkali-activated Cementitious Materials for Geothermal Wells

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Keywords

CMC, alkali-activated cement, self-degradable admixtures

ABSTRACT

Sodium carboxymethyl celluloses (CMC) can be used in the sodium silicate-activated slag/Class C fly ash cementitious material for geothermal well for its temperature decomposition. However, different CMC may have different application performance. Four kinds of CMCs with different molecular weights was experimented to confirm that CMC had an influence on the filtration properties, hydration products and compressive strength of alkali activated slag/ fly ash cement-based materials. Besides, the thermal degradation properties of CMC, the compressive strength and microstructure of the cement containing CMC were checked to evaluate the potentiality of starches as self-degradable admixtures. The analysis showed that: 1) all the CMCs had the effects of increasing the apparent viscosity of cement slurry, prolonging the setting time and reducing the static fluid loss on the alkali activated cement materials (AACM); 2) 4-CMC decreased the compressive strength of cement as the cement structures loosened after being heated and immersed in water for 24 h, and it had the most potentiality as a geothermal cement self-degradable admixture.

1. Introduction

Cement is one of the most commonly materials for using cementing and plugging in geothermal well. At present, many kinds of biopolymer materials can be used as additives of self-degradable

cement, including starch, PLA and CMC. Sugama *et al.* (2010, 2011, 2015) have already studied CMC generates carbon dioxide and acetic acid gas at high temperature to promote the self-degradation of AACM cement. CMC has good fluidity, which is often used as filtrate reducer in drilling fluid, so as to improve the performance of drilling fluid (Shang, 2005; Li, 2007; Li, 2011; Ying, 2003; Wang, 2009). When the PLA is added to the alkali activated slag fly ash cement (Tan *et al.*, 2016), the cement can effectively plug the cracks in the drilling process of 85 °C, and promote self-degradation of 200 °C -heated sodium silicate-activated slag/Class C fly ash cementitious material after contact with water.

This paper evaluates the effects of four kinds of CMCs on the properties of alkali activated cement materials (AACM), which include the apparent viscosity at room temperature, the static fluid loss at medium pressure and room temperature, the compressive strength after curing at 85 °C and the hydration products. In addition, the thermal degradation properties, the compressive strength and microstructures of 85 °C-curing cement after 200 °C-heating were studied to evaluate the potentiality of different CMCs as self-degradable admixtures.

2. Materials and Methods

2.1 Materials

The four different sodium carboxymethyl celluloses (CMCs) evaluated for their ability to degrade sealing material were supplied by Henan, Xinxiang; Shen Guang edible Chemicals Co. Ltd. (Shanghai, China); Xilong Chemical Co. Ltd. (Xilong, China) and Sinopharm Chemical Reagent Co. Ltd. The Class C fly ash was supplied by Luyuan Power Resource Development Groups Co. Ltd. (Dongying, China). Sodium silicate was supplied by Qingdao Yousuo Chemical Technologies, Inc. (Qingdao, China). The chemical compositions of slag and fly ash detected by inductively coupled plasma-atomic emission spectrometric (ICP-AES) are shown in Table 1.

Table 1. The chemical compositions of slag and fly ash detected by ICP-AES.

	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O
Slag	30.92	16.57	37.36	0.36	9.01	0.41	0.89	0.51
Fly ash	37.33	20.42	17.70	4.93	1.96	1.18	0.79	0.06

The AACM formula had slag/Class C fly ash ratio of 80/20 by weight, 6% sodium silicate by total weight of the dry pozzolana cement. The AACM without any CMCs was considered as control sample. The four kinds of CMC, 1-CMC, 2-CMC, 3-CMC and 4-CMC were added into AACM by the total weight of pozzolana cement. In preparing cement slurry with similar consistency, the water/blend (w/b) ratio depended on the particular CMC; namely, the ratio was 0.7 for 1.2% and 1.6% of 4-CMC and 1.6% of 3-CMC, the ratio was 0.6 for all other groups. Higher molecular weight CMCs increased slurries' viscosities and required larger water amounts to be mixable. AACM with 0.4%, 0.8%, 1.2% and 1.6% of four kinds of CMCs were cured in air at room temperature for 72 h, afterwards, all set cements were cured at 85 °C for 24 h (85 °C-cured). In addition, all cement were further heated for 24 h in an oven at 200 °C (200 °C-heated), and then immersed in water for 24 h. The CMC powders (0.5 g) were immersed into filtrate (3 mL) obtained by an API filter tester from control slurry. The filtrates with CMC were cured at room temperature for 72 h and at 85 °C for 24 h, and then filtered, washed, and dried for further testing.

2.2 Measurements

The viscosity-average molecular weight (MW) of the four kinds CMCs were measured by Ubbelohde viscometer.

The apparent viscosities at different rotational speeds of cement slurries containing 1.2% 1-CMC, 2-CMC, 3-CMC and 4-CMC, respectively, were measured on a Brookfield viscometer (Brookfield 8542373, USA).

The fluid loss of slurries of control and AACM with 0.4%, 0.8%, 1.2% and 1.6% CMC at room temperature medium pressure (RTMP 20 °C and 0.69 MPa) were respectively carried out on API Filter Tester (Haitongda 92 GGS42-2, China).

Compressive strength was tested according to Chinese National Standard GB 10238-2005 (AQSIQ and CNSA, 2005) and (CNEA, 2010) Chinese Petroleum and Natural Gas Industry Standard SY/T 6544-2010 on a servo universal testing machine (Chandler YAW-300B, Chengdu, China) with a loading rate of 17.1 kN/min. The cube samples with the size of 50.8 × 50.8 × 50.8 mm (2 in × 2 in × 2 in) were cast. Three cubic specimens of each composition were prepared to measure the compressive strength.

Powder X-ray diffraction (XRD) carried out on a diffractometer (Rigaku D/max, Tokyo, Japan) was employed to identify the crystalline phases of the 200 °C-cured sample. The samples were crushed, ground and passed through a mesh screen. The scanning regions were between 2θ values of 3 ° and 70 °, at a resolution of 0.02 ° / step.

The thermal degradation properties of non- and filtrate-treated CMCs were checked on a Thermo Gravimetric Analyzer (TA instruments Q600, New Castle, DE, USA) under a nitrogen atmosphere with the temperature range from a room temperature of ca. 20.0 °C to 600.0 °C at a heating rate of 10.0 °C / min.

The microstructures of AACM with 1.2% different CMCs immersed in water for 24 h were observed on a Scanning Electron Microscopy (FEI XL30SFEG, Hillsboro, OR, USA) running at an accelerating voltage of 20 kV.

3. Results and discussion

3.1 CMCs

1g CMCs were dissolved in 200g water, the viscosity of the solution was shown in Figure 1. The pH of these solutions fluctuates was between 7.96 and 8.15. The molecular weight of 1, 2, 3, 4-CMC was 739957.6, 1859684, 2062141 and 3875773, respectively measured by the Ubbelohde viscometer. It shows that the molecular weight of CMC and viscosity were positively correlated.

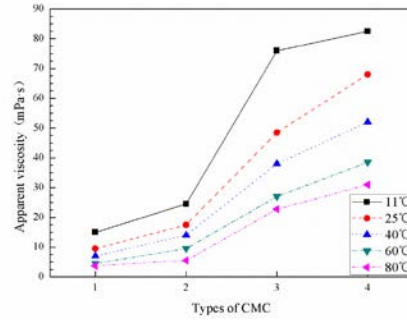


Figure 1: The figure above is in viscosity curves of four kinds of CMC at different temperatures.

3.2 Cement viscosity

Good flow performance plays an important role in the wider application of cement. The mud added CMC has better fluidity. The four kinds of CMCs have an increased effect on the viscosity of the cement. When the test speed was 10 r / min and 50 r / min, the apparent viscosity of the slurries containing 1.2% CMCs were 2789 and 1416 mPa · s, 3959 and 1932 mPa · s, 9628 and 5837 mPa · s, 13572 and 8678 mPa · s respectively. The order of increasing the viscosity of cement paste was 4-CMC > 3-CMC > 2-CMC > 1-CMC. The apparent viscosity of the cement slurry decreases rapidly as the speed increases.

When the rotor speed increased from 1 r / min to 100 r / min, the apparent viscosity of the slurry containing 1.2% 4-CMC was decreased from 39891 mPa · s to 5209 mPa · s , the apparent viscosity of the slurry containing 1.2% 3-CMC was decreased from 34793 mPa · s to 4196 mPa · s, and 1.2% 2-CMC from 11398 mPa · s to 1386 mPa · s; 1.2% 1-CMC from 8998 mPa · s to 1185 mPa · s; While Control dropped from 4799 mPa · s to 198.0 mPa · s. As the test speed increased, the most significant reduction of the apparent viscosity was cement slurry containing 4-CMC.

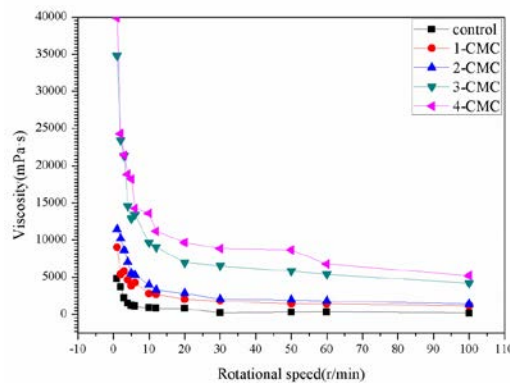


Figure 2: The figure above is in apparent viscosity of cement slurries containing 1.2% of four CMCs at different rotational speeds.

3.3 Static fluid loss

In cementing operations, a large fluid loss of cement leads to a massive losing of water, which slows down the hydration to decline the strength, and thus has negative influence on cementing quality (Li, 2015). With the addition of CMC to the AACM, w/b was increased and the fluid loss was reduced.

Figure 3 plots the values of filter loss at RTMP. The test conditions of RTMP are room temperature and 0.69 MPa for 7.5 min, the static fluid loss of cement slurries as Figure 3. The RTMP fluid loss was decreased by 26.0%, 22.8%, 60.5% and 66.8%, respectively, as the addition 1.2% 1-CMC, 2-CMC, 3-CMC, 4-CMC, when compared to control. Among these four CMCs, 4-CMC has the greatest decrease effect on fluid loss at RTMP.

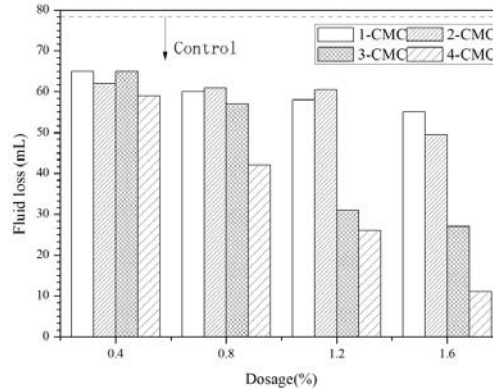


Figure 3: The static fluid loss of control and AACM with different dosages of four kinds of CMC.

3.4 Compressive strength

It can be seen from Figure 4 that the compressive strength decreases as the amount of CMC increases. For 1-CMC, the change in compressive strength is small, indicating that the smaller the CMC molecular weight, the smaller the effect of the amount on the compressive strength. For 1, 2 and 3-CMC, the compressive strength changes little with the dosage of 1.2% and 1.6%, and for 4-CMC, the compressive strength does not meet the standard requirements with the dosage of 1.6%, which means CMC dosage of 1.2% is the optimal dosage.

As shown in Figure 5, the compressive strength declined with an increase in CMC viscosity, because as the viscosity increases the water demand increases. In fact, when adding 1-CMC, the water-to-blend ratio is 0.6, adding 4-CMC, the water-to-blend ratio is 0.7, and under different curing conditions, the compressive strength of 4-CMC generally lower than 1-CMC by about 50%. For the drilling operations to resume after curing circulation losses the accepted compressive strength is 3.5 MPa. Even the lowest compressive strength achieved with the 4-CMC was more than sufficient for plugging the fractures and resuming the drilling.

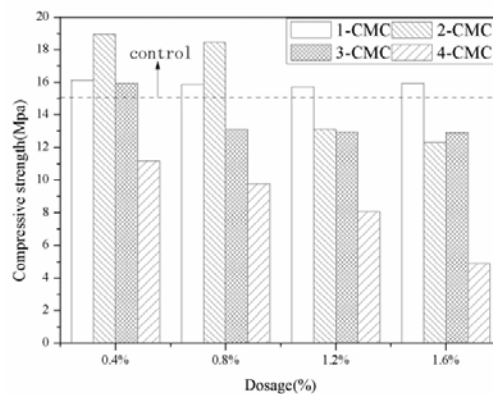


Figure 4: Compressive strength of 85 °C-autoclaved sealers with different dosages

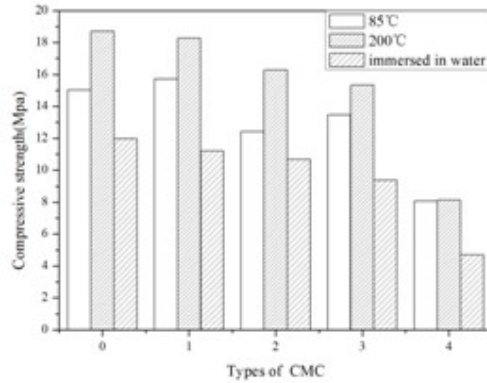


Figure 5: Compressive strength under different curing conditions with 1.2% CMC

3.5 TGA study

One of the necessary factors to promote cement self-degradation is the generation of volatile gases, CMC can degrade generated CO₂ and acetic acid at high temperature. If the rate of these gases is high enough, the degradation of the cement can be promoted.

Figure 6 is the TGA curves for non-treated CMC, all TGA curves are very similar. It can be seen that the thermal decomposition stage of CMCs were mainly between 200 °C -275 °C. At 600 °C, the loss of CMCs were 42.8%, 70.2%, 59.7% and 61.6%, respectively.

Figure 7 shows the TGA curves for pore solution-treated CMC at high temperature, Compared with Figure 6, there were three differences as follows: first, the main section of weight loss was between 25 °C and 275 °C; second, from 300 °C to 600 °C, the rate of loss was higher than untreated; and, third, the loss of CMCs were 37.0%, 50.1%, 47.4% and 49.8% at 600 °C, respectively, which were 13.5%, 28.6%, 20.6% and 19.2% lower than the untreated losses.

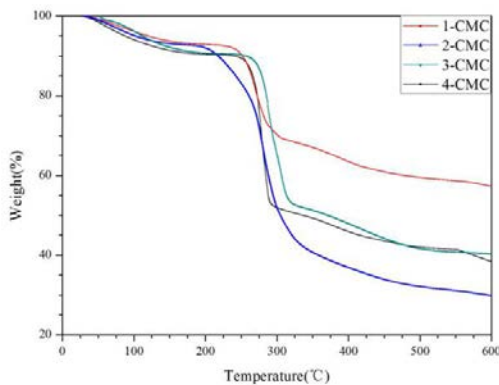


Figure 6: TGA curves for non-treated CMC

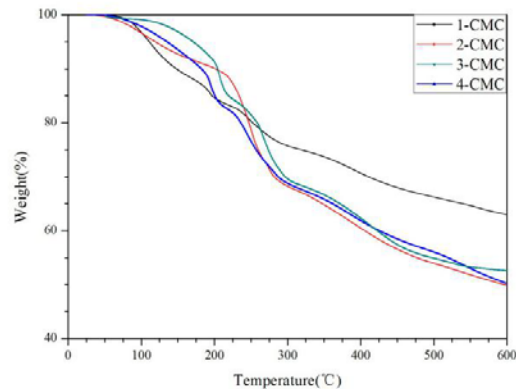


Figure 7: TGA curves for pore solution-treated CMC

Figure 8 shows the loss in weight rate of non-treated CMC, which was the integral for the X axis in Figure 6. It can be seen that the main stages of the loss were between 225 °C and 300 °C, and the maximum loss rate was 4-CMC, the smallest was 1-CMC. Therefore, during thermal degradation, the larger the MW of CMC, the greater the loss rate, the more volatile gas produced,

resulting in increased porosity of the test block, and thus the ability to promote the self-degradation of alkali-activated cement.

Figure 9 shows the loss in weight rate of pore solution-treated CMC, which was the integral for the X axis in Figure 7. It can be seen that the main stages of loss in weight of 4-CMC were at 175-200 °C and 225-300 °C. The loss stage of 2-CMC was mainly between 200 °C and 300 °C, while 1-CMC was smaller than 2 and 4-CMC. Compared with Figure 8, the loss of non-treated CMC was concentrated at 225-300 °C, and the loss rate was much larger than that of pore solution-treated CMC. While, at other temperatures, the rate of loss of pore solution-treated CMC was greater than that of non-treated.

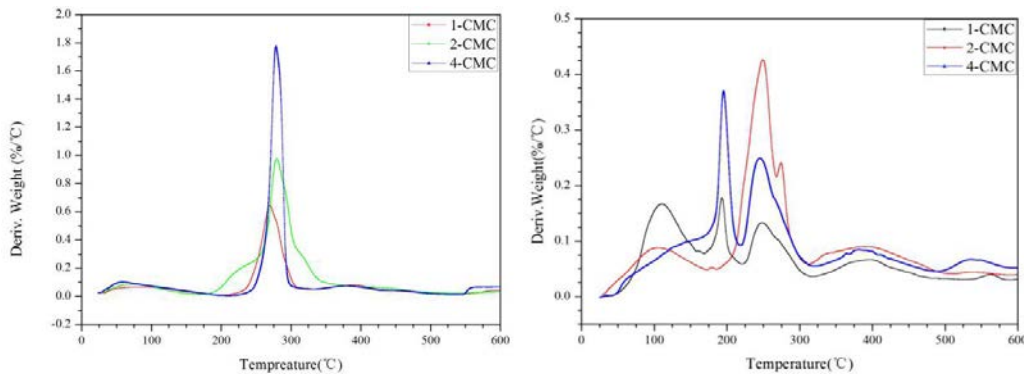


Figure 8: Loss in weight rate of non-treated CMC

Figure 9: Loss in weight rate of pore solution-treated CMC

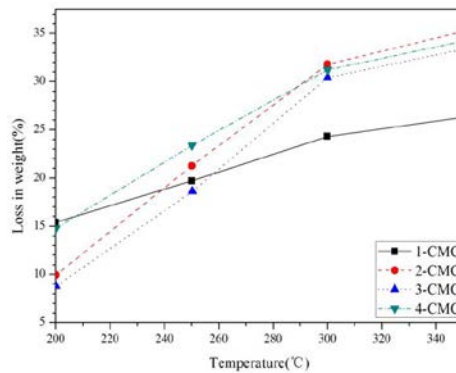


Figure 10: Loss in weight of pore solution-treated CMCs at temperatures 200-350 °C

3.6 XRD analysis

Figure 11 shows the XRD patterns of 200 °C-cured specimens of the control and with different CMC dosages. It can be seen that, each XRD pattern exhibits an amorphous hump between 2θ values of 29 ° and 30 °. This is because the maximum value of the Calcite - CaCO_3 phase appears at $2\theta = 29.430^\circ$, Quartz - SiO_2 appears at $2\theta = 30.976^\circ$, and two peaks were superimposed on each other. It indicated that there were a lot of quartz and calcite appearing at this time.

Comparing the height of the peak and the area surrounded by the diffraction peak, we can see that the order of decreasing the area was: 4-1.2 < 2-1.2 < Control < 3-1.2 < 1-1.2, which means that the degree of response also decreased.

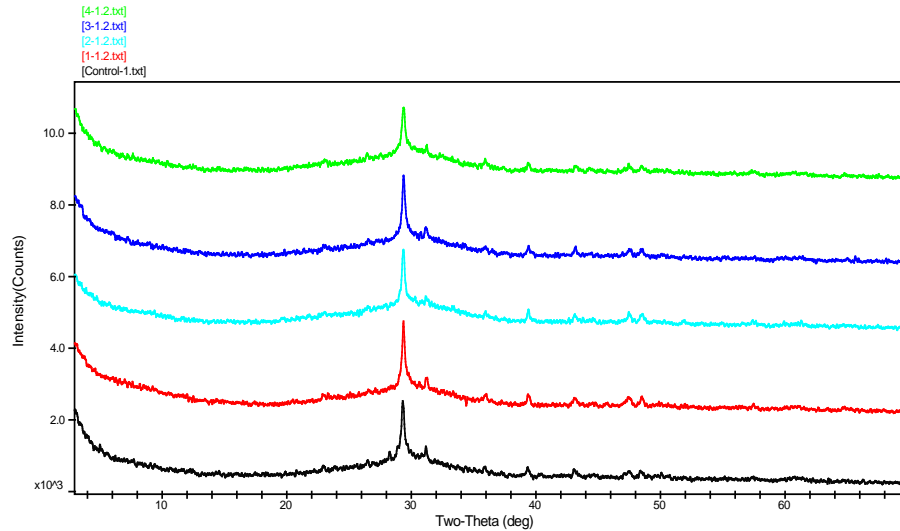
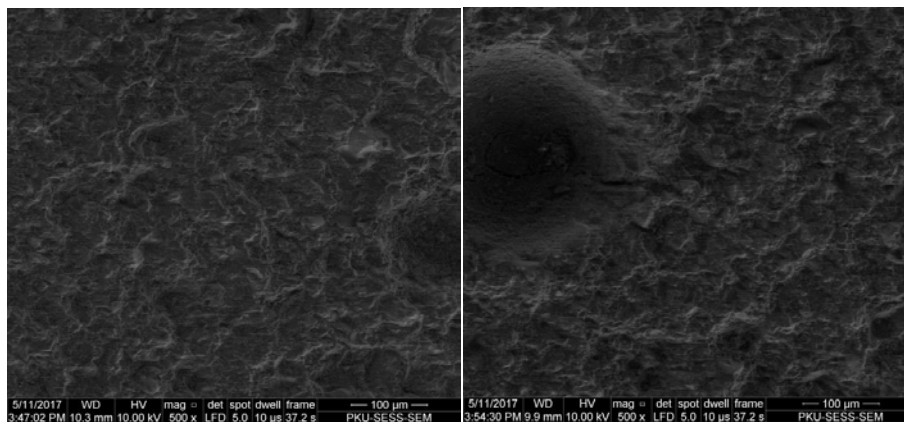


Figure11: XRD patterns of 200 °C-cured specimens of the control and with different CMC dosages

3.7 SEM

Figure 12 shows the images of the section of heated samples after immersed in water for 24 h: (a) the control; (b) 1-CMC; (c) 2-CMC; (d) 3-CMC; (e) 4-CMC. The most compact structure is Control, followed by 1-CMC, internal pores appear in 2 and 3-CMC, while pores and cracks can be seen in the 4-CMC obviously. Combining the results of compressive strength and the results of the TGA curves, the strength of the cement is closely related to the microstructure of the cement. The density of the structure directly affects the strength of the size of the loose internal structure will lead to decreased strength. And TGA curves shows that the filtrate-treated CMC has a weight loss after heating. That is, alkali-activated cement inside the CMC after heating gas generated weight loss, CMC changes lead to loose structure of cement. After immersed in water, the material inside the cement began to partially dissolve. Resulting in a more loose structure of cement indicated a rapid decline in compressive strength. Moreover, taking into account of the conservation of 85 °C, the compressive strength of cement added 4-CMC is the largest. Therefore, 4-CMC has the greatest potential for geothermal cement self-degrading additives.



(a)

(b)

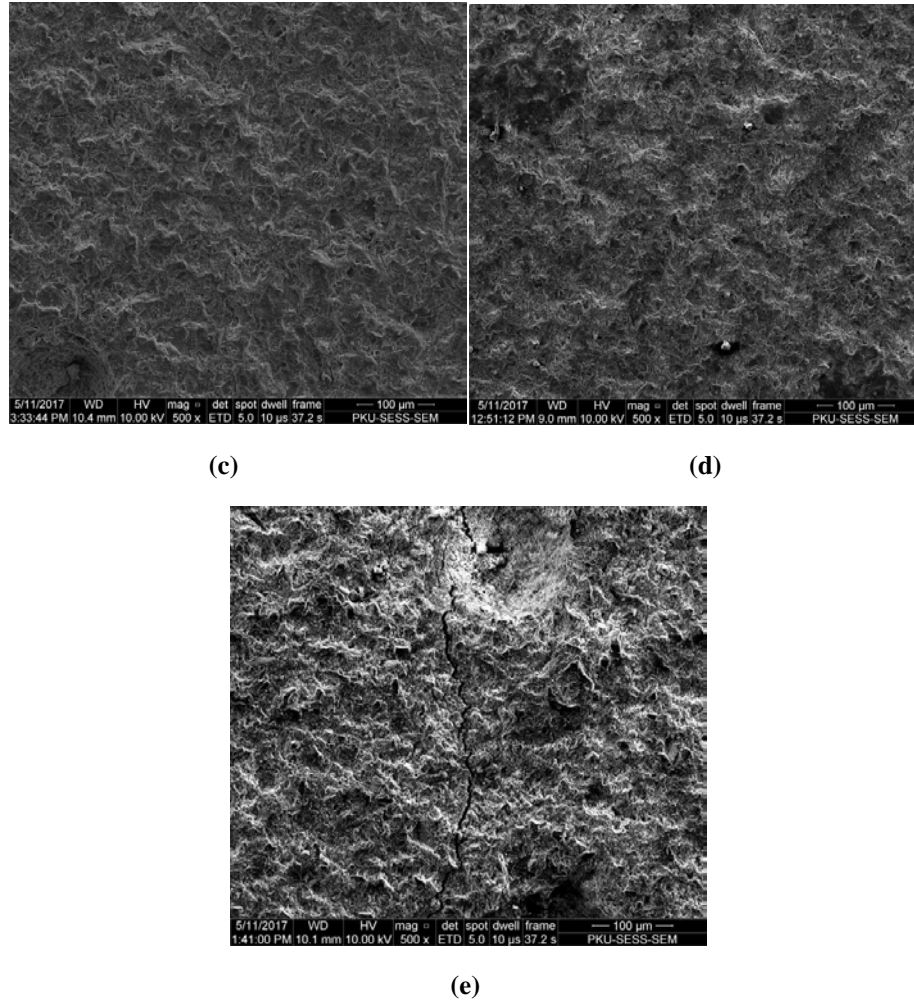


Figure 12: Images of the section of heated samples after being immersed in water for 24 h:

(a) the control; (b) 1-CMC; (c) 2-CMC; (d) 3-CMC; (e) 4-CMC.

4. Conclusion

- a) The four kinds of CMCs have effects of enhancement on the cement slurries viscosity. The sequence of enhanced effect of CMCs on cement viscosity is as follows: 4-CMC > 3-CMC > 2-CMC > 1-CMC. The greater the molecular weight, the more obvious the viscosity of cement.
- b) Among these four CMCs, 4-CMCs has the greatest decrease effect on fluid loss in the conditions of RTMP. And the effect increases as the 4-CMC dosage increases.
- c) The highest tested molecular weight CMC (4-CMC) added at 1.2% by weight of blend has the lowest compressive strength of cement specimens.
- d) The thermal degradation of 4-CMC made the structures of 200 °C-heated cement looser, and then the dissolution of compositions in cement became faster, presenting as the decrease of compressive strength and appearance of cracks. Therefore, the highest tested molecular weight CMC (4-CMC) added at 1.2% by weight of blend was the most efficient in promoting cement self-degradation among the tested products.

5. Acknowledgement

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