- Technical Report -

DEGRADATION RESISTANCE OF CEMENT MORTAR SUBMERGED IN VARIOUS OILS

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ABSTRACT

The aim of this study is to evaluate and analyze the degradation resistance of cement mortar under the conditions of submerged in various oils. Although former research reported oil can damage the cement-based materials, it was not sufficiently known regarding detail mechanisms and different degree of damages depending on various oil types. In this research, to evaluate the influence of various oil types on degradation and degradation resistance of cement mortar, various types of oils were used available in general market. According to the experiment, depending on oil types, the degree of degradation was vary, especially, biodiesel was found as the most harmful for cement mortar in this research conditions.

Keywords: concrete durability, fatty acid, oil, expansive collapse of cement mortar

1. INTRODUCTION

Concrete structures are located many different environmental conditions [1,2] from severe temperature conditions to ingression of chemical substances such as chloride, sulfate, and NO_x or CO_x. Furthermore, as the usage of concrete structure has been increased concrete structure has chance to contact with not only environmental factors but also artificial factors. In aspect of durability of concrete structure, these environmental and artificial factors can influence of concrete performance and furthermore decrease the life span of concrete structure.

Oil, mainly consisted with fatty acid is one of the most widely used liquid and thus it can be contacted or spilled on the surface of concrete structure during construction or operation. Additionally, considering constructing silo with concrete, the concrete structure can be contacted with oil so long time period. According to the former research, especially, Mizugami's report [3] (see Figure 1), cement-based materials can be collapsed by chemical expansion when it reacts with fat or oils. This reaction is so called "saponification", the reaction of making fatty acid salt and glycerin by reaction between alkali and fatty acid. From this reaction, the reaction product of fatty acid salt can be expanded [4], and thus in concrete microstructure, specially, capillary pores, excessively expanded fatty acid salt can be considered as a reason of collapse of the cement-based materials. Namely, it can be summarized that because of strong alkali in concrete's capillary pore produced by $Ca(OH)_2$ can react with oil or fatty and damages the microstructure of concrete.

However, although the degradation caused by oil or fat is not so often observed or reported, there was no enough information or report on the degradation of concrete or cement-based materials depending on types of oil or fat, degradation mechanisms, and collapsing pattern. Therefore, in this research, to provide a fundamental information regarding degradation of cement-based materials with oils, the degradation of cement-based materials was evaluated under the conditions of submerged in various types of oil with assuming the situation of oil spilling on the mortar finished floor and remained a long time period was assumed. From the results of this research, it is expected to contribute on providing the fundamental idea of degradation of cement-based materials including concrete by reaction with various types of oil.

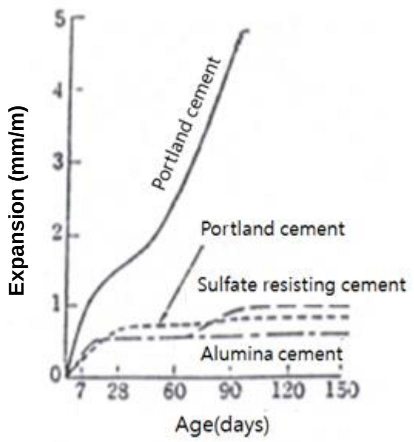

Figure 1. Expansion of various cement-based materials submerged in oil (all specimens were mortar phase of water-to-cement ratio 0.55 and cement to sand of 1 to 6) by Mizugami [3]

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2. EXPERIMENT

2.1 Experimental Plan

In this research, to evaluate the degradation of cement-based materials submerged in various types oil, the experiment was designed as shown in Table 1. First of all, all specimens were mortar phase. The experiment was designed not only changing oil types but also mortar conditions: for mortar specimens, three different cement to sand ratios with three different water-to-cement ratios were prepared to simulate the performance of cement-based materials related with capillary porosity. All three different mix designs are shown in Table 2. To secure the enough workability for practical conditions, all mixtures were designed to satisfy the 150 ± 25 mm of slump flow. As a control factor, five different types of oil were prepared. Regarding the mixtures, fundamental properties regardless oil submerging, and degradation performance related with oil were conducted. As the tests on fundamental properties, flow, and unit mass of fresh state mixtures were measured. As a hardened properties of the mixture, compressive strength was measured at 3, 7, 28, 90 and 180 day-age. After submerging oils, as a degradation performance tests, the length change, and mass change of mortars were measured and compressive strength was measured at 180 day-age.

2.2 Materials and sample preparation

In this research, all materials used were generally used and available in South Korean market. Ordinary Portland cement (OPC) used in this research was similar properties of Type I cement from ASTM C150 [5], and the physical properties of OPC is shown in Table 3. For mortar mixture, fine aggregate used was a crushed sand obtained from a single source in South Korea and its physical properties are provided in Table 4. For mixing, tap water was used as a mixing water. There was no additional chemical admixture for mixtures except oils. The oils used were five different oils available from South Korean market. For edible oils, soybean oil (SO), grape seed oil (GR), and lard (LA) were prepared, and for industrial oils, biodiesel (BD), and hydraulic fluid (HF) were prepared. All oils actually used are shown in Figure 2, and their physical properties are provided in Table 5.

In this research, the specimens were produced with 40 mm width, 40 mm depth, and 160 mm length of mortar bar. The cement mortar was mixed by ASTM C305 [6] protocol. The mixed cement mortars were molded by the mold with prefixed size and cured for one day in lab conditions of 20 ± 2 °C and R.H. (60 ± 5) %. After one day, the specimens were demolded and wet cured for six days followed by 21 days of air curing. For oil submerging, the mortar specimens were submerged in five different oils for 152 days (total time period of 180 days after mixing). Specially, in the case of lard, since it was a solid at ambient conditions, a piece of lard was heated and melted to submerge the mortar bar. After submerging the mortar bar in liquidized lard, the sample was stored at general lab conditions. The detail time frame for sample preparation is shown in Figure 3.

Table 1. Experimental plan

Mixture	Code	M1	M2	M3
	C : S*	1 : 1	1 : 3	1 : 5
	W/C**	0.40	0.60	0.80
	Target flow (mm)	150 ± 25		
	Type of oil	• Control (water) – WA • Soybean oil – SO • Grape seed oil – GS • Lard – LA • Biodiesel – BD • Hydraulic fluid - HF		
Tests	Fundamental properties	• Flow • Unit mass • Compressive strength (@ 3, 7, 28, 90, and 180 d)		
	Degradation performances	• Length change • Mass change rate • Compressive strength (@ 180 d)		

*C : S means cement to sand ratio
**W/C means water-to-cement ratio

Table 2. Mix design

Code	C : S	w/c	Unit content (kg/m^3)*		
			Water	Cement	Sand
M1	1 : 1	0.40	364	910	910
M2	1 : 3	0.60	293	488	1465
M3	1 : 5	0.80	267	333	1666

*Unit content of each material is the mass required for one m^3 of mortar mixture.

Table 3. Physical properties of cement

Specific gravity	Blaine (cm^2/g)	L.O.I (%)	Setting time (min.)	
			Initial	Final
3.15	3450	2	275	325

Table 4. Physical properties of fine aggregate

Density (g/cm^3)	Absorption rate (%)	Fineness modulus
2.70	1.13	2.60

Figure 2. The actual photo of oils used

2.3 Test methods

All tests conducted in this research were followed by generally known method and JIS standards. For fresh

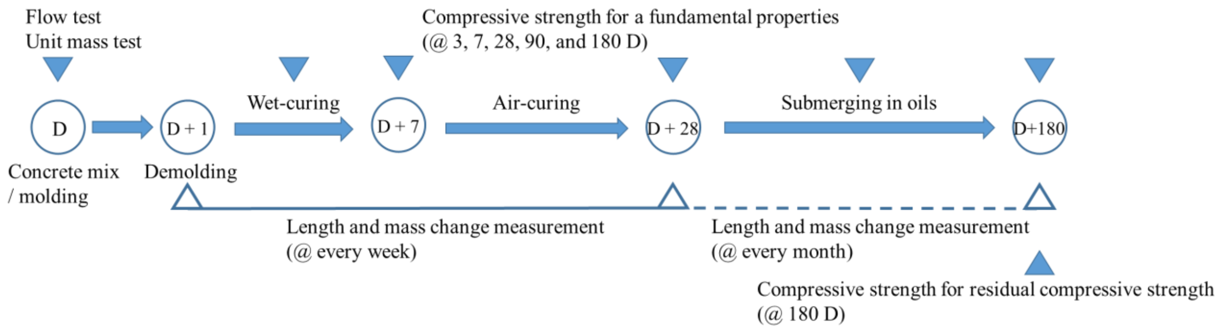


Figure 3. Experimental timeframe

Table 5. Physical properties of submerging liquid

Type*	Appearance	
	Color	Phase
WA	None	Liquid
SO	Yellow	Liquid
GR	Yellow	Liquid
LA	White	Solid
BD	Pale yellow	Liquid
HF	Pale yellow	Liquid

Type	Properties		
	Density (g/cm^3)	Viscosity (Pa.s)	Saturated fat (%)
WA	0.998 (@20°C)	0.001 (@20°C)	0
SO	0.820 (@20°C)	0.051 (@20°C)	14
GR	0.915 (@20°C)	0.012 (@20°C)	11
LA	0.918 (@40°C)	0.065 (@40°C)	41
BD	0.884 (@20°C)	0.015 (@20°C)	97
HF	0.842 (@15°C)	0.146 (@15°C)	1.2

*WA: water, SO: soybean oil, GR: grape seed oil, LA: lard, BD: biodiesel, HF: hydraulic fluid

Table 6. The fundamental properties of mortar mixtures

Mixture	Fresh state	
	Flow (mm)	Unit mass (kg/m^3)
M1	145	2288
M2	175	2248
M3	165	2268

Mixture	Compressive strength (MPa)				
	3 D	7 D	28 D	90 D	180 D
M1	45	50	69	72	79
M2	13	21	36	38	41
M3	6	9	22	22	22

state properties, flow test was conducted by KS L 5111, and unit mass was measured by JIS A 1116. For hardened properties, compressive strength was measured by following JIS A 1108.

Degradation tests after submerging oils were executed by JIS standard. Although there was no standardized test method on the cement-based materials damaged by oil or fat, in this research, the degradation evaluation method of freeze-thawing damage was used because the damaging mechanisms were similar as an expansion. Therefore, to evaluate the degradation of mortar specimens, length and mass changes were measured. For length change of the mortar bar, the measurement was conducted by JIS A 1129, and the mass change of the mortar bar was calculated as a percentage as follow:

$$M_c = \frac{M_O - M_R}{M_O} \times 100\ (\%) \qquad (1)$$

where, M_c is mass change rate, M_O, and M_R are the original mass, and the reduced mass at certain time, respectively.

The measurements of length and mass changes were conducted every one week during the first month and executed every month after the first month until 180 day-age. After the 180 days' submerging, residual compressive strength was measured at 180 day-age following JIS A 1108.

3. RESULTS AND DISCUSSION

3.1 Fundamental properties of mortar

The fundamental properties of mortar is provided in Table 6 depending on mixture conditions (cement-to-sand ratio and water-to-cement ratio). All mixtures designed and mixed satisfied target properties in flow and unit mass. Also, according to the compressive strength results at each day, all mixtures developed compressive strength normally. Therefore, based on the fundamental properties, all mortar specimens were normal and there was no significant defect.

3.2 Degradation performance of mortar under oil submerging

(1) General trend of degradation of mortar bars

The shapes of the mortar bar after submerging oils are shown in Figure 4. As shown in the figure, the shape of the damaged mortar bar was similar to the mortar damaged by freeze-thawing action. It is considered that the reason is suffering the collapse of microstructure due to the expansion for both cases. Thus, it may the measuring length and mass change is appropriate to evaluate the degradation of mortar bar with oil submerging. As shown in Figure 4, the collapsed mortar bars were observed with certain types of oils: soybean (SO), lard (LA), and biodiesel (BD). Additionally,

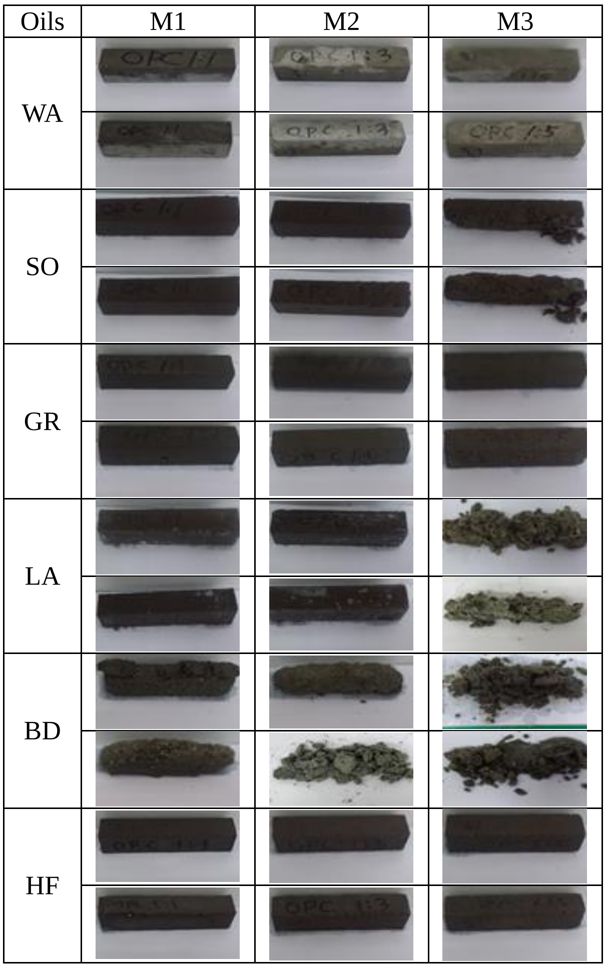
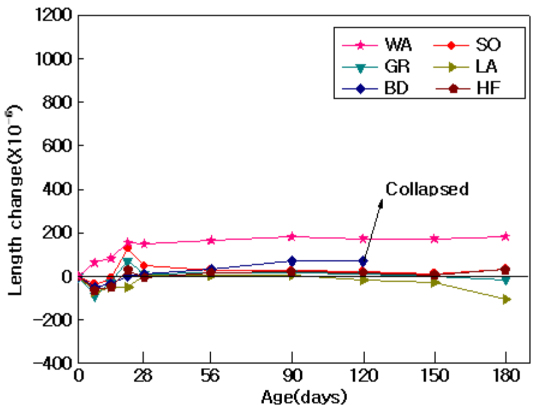


Figure 4. The shape of the mortar bar after submerging oils (For each case, two samples were tested.)

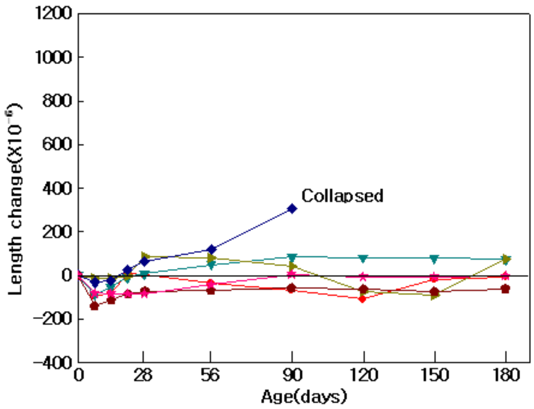
among the same oil, the mixture with higher water-to-cement ratio and less cement content showed severe damage than lower water-to-cement ratio and more cement content. From the damage shapes, biodiesel caused the most severe damage on mortar bar.

(2) Influence of type of oil and mixture on degradation of mortar bars

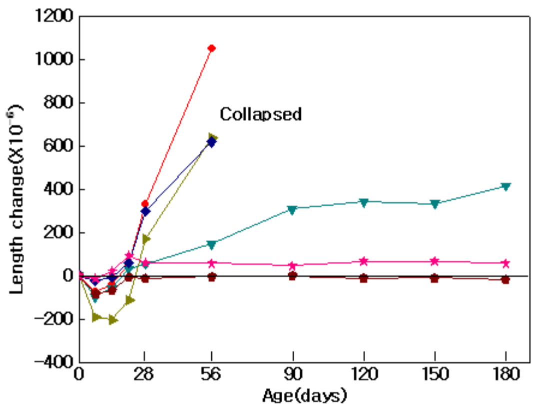
Comparing with the control mortar bar without any submerging in oil, the mortar bars submerged in five different oils were measured their length and mass changes. As shown in Figure 5, although most mortar bars experienced shrinkage until 28 day of standard curing, all mortar bars showed expansion after 28 day during submerging oils. Depending on the mixture conditions, the mortar bar with the lowest water-to-cement ratio and the largest portion of cement, showed the least degree of expansion for all cases except the control mixture submerged in water. From this result, it is considered that basically oil hardly intrude the microstructure of mortar when it has low water-to-cement ratio rather than water. Similar to this analysis, as the water-to-cement ratio of mortar mixture was increased, the mortar bars experienced more expansion. Additionally, depending on the type of oil, different results of length change was obtained. First of all, it can



(a) M1



(b) M2

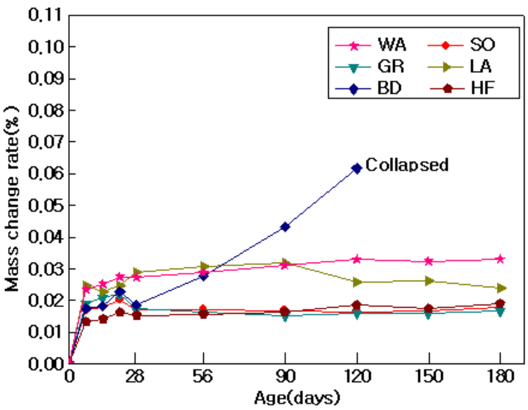


(c) M3

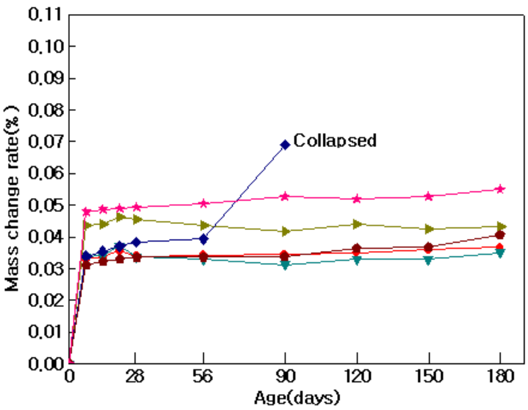
Figure 5. Influence of submerging oils on length change of the mortar bars

be clearly state that biodiesel is the most reactive oil with cement mortar. According to the Table 5 on physical properties of oils, the biodiesel has the relatively lower viscosity than other oils and the highest saturated fat among the oils used in this research. Therefore, because of low viscosity, biodiesel could be intruded into the capillary pore of mortar bar and it could occur the saponification with its large portion of fatty-acid.

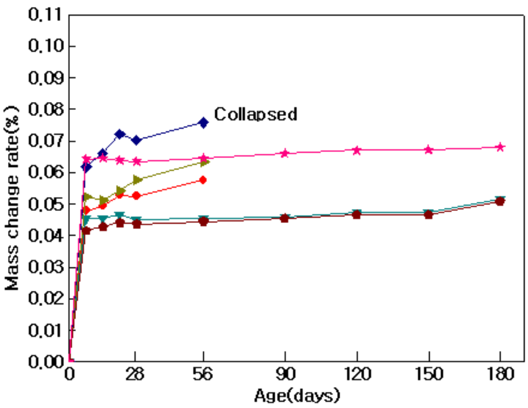
From the mortar with the highest water-to-cement ratio and the least portion of cement, except biodiesel, soybean oil, lard, and grape seed oil were caused expansion of the mortar bars. On the other hand, the hydraulic fluid did not cause any expansion of the mortar



(a) M1

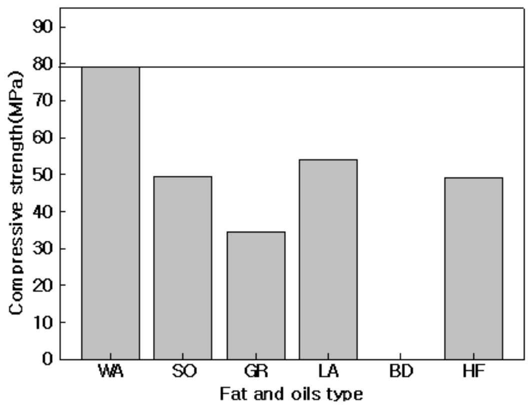


(b) M2

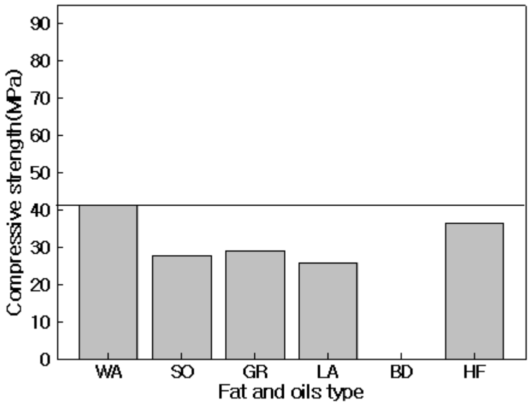


(c) M3

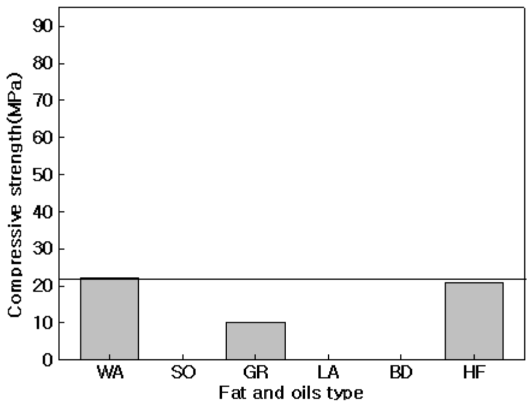
Figure 6. Influence of submerging oils on mass change rate of the mortar bars



(a) M1



(b) M2



(c) M3

Figure 7. Influence of submerging oils on compressive strength of the mortar bars

bar. It can be state that relatively high viscosity and less fatty-acid hindered intrusion into the capillary pore and saponification with alkali of cement mortar.

As shown in Figure 6, the mass change results also shows similar trend of length change. For all mixture conditions, biodiesel showed the most expanded result. Furthermore, as water-to-cement ratio was increased, the timing of mortar bar collapsing was accelerated. It is considered that with fast intruding speed with high capillary porosity, saponification and expansion of fatty acid salt are accelerated. Generally, from the mortar bar of water-to-cement ratio 0.40 and 0.60 mixtures showed constant mass changing rate which means there was no further expansion after the first reaction and expansion. However, for the mortar bar of water-to-cement ratio 0.80 mixture, not only biodiesel, but also lard and soybean oil produced increasing mass changing rate. From this result, it can be state that less dense microstructure with higher water-to-cement ratio provides more specific area to be reacted with intruded oil.

3.3 Analyzing residual compressive strength

To evaluate the damage of microstructure due to the expansion, residual compressive strength was measured after the submerging. Figure 7 shows the compressive strength of the mortar bars depending on

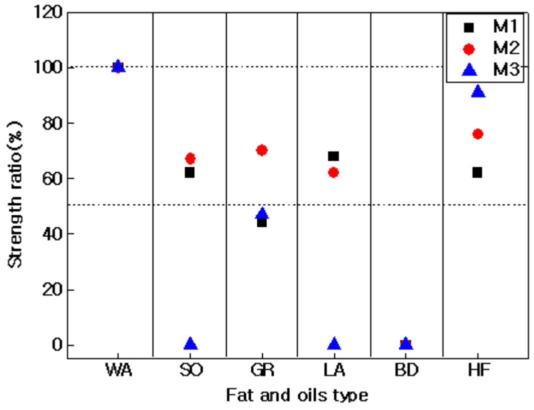


Figure 8. Correlation between types of oil and residual compressive strength (assuming the compressive strength of control mixture to 100 %)

different mixture conditions and submerged oils. Comparing with the control mortar bar submerged in water (WA), all mortar bars submerged in oils decreased compressive strength. Especially, the mortar bars submerged in biodiesel could not be measured compressive strength because they were collapsed regardless mixture conditions. Similar to length and mass changing results, hydraulic fluid influenced less effect on compressive strength than any other oils.

Figure 8 shows correlation between oil types and residual compressive strength. The residual compressive strength was calculated by assuming the compressive strength of control mortar bar to 100 %. As shown in the figure, generally for the mixtures with 0.40 and 0.60 of water-to-cement, the compressive strength was decreased about 40 to 50 %. In the case of the mortar bar with 0.80 of water-to-cement ratio, all mortar bars except the mortar bars submerged in grape seed oil (GS) and hydraulic fluid (HF) suffered collapse. Specially, the mortar bar submerged in grape seed oil (GS) showed approximately 50 % of reducing compressive strength.

4. CONCLUSIONS

In this research, with the goal of providing a fundamental idea about degradation of cement-based materials including concrete when they are submerged in oil or fat. To evaluate the degradation behaviors of cement-based materials, generally market-available oils were tested and the results can be summarized as follow:

(1) When a mortar bar was submerged in oil or fat, some mortar bar suffered collapse and the pattern of collapse was the self-collapse due to the expansion. This expansion is considered as a result of producing fatty acid salt or soap by saponification in capillary pore.

(2) Depending on the mixture conditions, the expansion by saponification can be vary: in this research conditions, the mortar bar with lower water-to-cement ratio experienced less expansion. This is considered to be related with capillary pore due to the different degree of hydration.

(3) Different types of oil made different degree of expanding damage of the mortar bar. Among the five oils used in this research, biodiesel showed the most severe expanding damage on mortar bar. According to the physical properties of oils, low viscosity and high portion of saturated fat can be the factors on causing expansion of mortar bar by saponification.

(4) Although there was no significant damage from observation, from the residual compressive strength, all mortar bars suffered decreased compressive strength after the oil submerging, although there was different degree of degradation.

Summarizing above, when the cement-based materials submerged in various oil or fat, they can be collapsed by microstructural damage due to the expansion. This microstructural expanding damage is related with intrusion of oil and reactivity with alkali, in this research conditions, biodiesel showed the most harmful oil with low viscosity and large portion of saturated fat. Additionally, the conditions of cement-based materials can be influence on degradation of cement-based materials: higher capillary pore caused by higher water-to-cement ratio contributes higher degree of degradation. Therefore, from this research, a fundamental conditions of cement-based mixture and features of oil to be related with degradation due to the expansion is provided.

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