DURABILITY OF ULTRA-HIGH PERFORMANCE CONCRETE IN NH_4NO_3 SOLUTION

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***Summary**: The present study assessed the workability, compressive strength, density and NH_4NO_3 resistance of ultra-high performance concrete (UHPC) with different contents of rice husk ash (RHA), silica fume (SF) and ground granulated blast-furnace slag (GGBS). With the same water and superplasticizer content, workability and compressive strength of UHPC containing RHA are similar to those of UHPC containing SF. The density of UHPC containing RHA at the age of 7 days is slightly higher than that of UHPC containing SF. With increasing of hydration time (28 days), the refining effect of SF on the microstructure of UHPC is more significant than that of RHA. Therefore, the SF-modified mixture possesses a higher density compared to the RHA-modified one. The deterioration of UHPC containing RHA in the NH_4NO_3 solution is more severely than that of UHPC containing SF. The combination of GGBS and RHA or SF was found to improve the properties of UHPC.*

***Keywords**: UHPC; rice husk ash; GGBS; silica fume; NH_4NO_3 resistance.*

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1. Introduction

Ultra-high performance concrete (UHPC) is a new type of concrete with 28d-compressive strength over 150 MPa and advanced durability properties that has gained a strong interest in research and application in recent years [1-2]. To optain the outstanding properties, UHPC commonly consists of a high amount of Portland cement, puzzolanic admixtures and fine grained aggregates and with a high dosage of superplasticizer [3-5]. The main objectives of researches are not only to improve compressive strength, ductility, microstructure and durability of concrete but also to enhance the workability, to reduce the cost and to make UHPC more sustainable. The price of concrete is now not the cost of 1 m^3 concrete but rather the cost of 1 MPa or 1 year of life cycle of a structure. It is necessary to take into account the final cost of UHPC and, above all, of the produced constructions [6].

Previous studies [7-8] showed that with the mesoporous structure, the water absorption capacity of rice husk ash (RHA) is significantly higher than that of silica fume (SF). It can absorb an amount of free water in RHA-blended Portland cement mixture to improve compressive strength. The absorbed water in the porous structure allows Ca^{2+} ions to diffuse into internal parts of RHA particles to enhance the pozzolanic reactivity of RHA and maintains the hydration of cementitious materials [7]. However, the portlandite content in RHA-modified matrix is still higher than that in SF-modified matrix.

UHPC can be produced by using RHA to completely replace SF [9-11]. The combined utilization of ground granulated blast-furnace slag (GGBS) and RHA or SF in UHPC production enhances the workability and compressive strength of UHPC [9-10]. The durability in aggressive conditions of UHPC containing different puzzolanic admixtures needs more detailed investigations. The present study investigates workability, compressive strength, porosity and durability in NH_4NO_3 5M of four UHPC mixtures containing different contents of RHA, SF and GGBS.

2. Materials and methods

2.1 Materials

Cementitious materials used in this study were ordinary Portland cement (CEM I 52.5 R-HS/NA conforming to DIN EN 1164-10), GGBS, RHA and undensified powder of SF. Quartz powder and quartz sand

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were utilized as filler and aggregate, respectively. Chemical compositions and physical properties of the materials are given in Table 1 và Table 2. The RHA is a kind of mesoporous amorphous siliceous material with 87.4 wt.-% SiO_2 content (Table 1), mainly amorphous phase calculated by quantitative X-ray diffraction (QXRD) analysis (Figure 1), i.e. 97.4 wt.-% amorphous, 2.0 wt.-% quartz and 0.6 wt.-% calcite and mesopores diameter about 2 to 50 nm (Figure 2). RHA possesses larger particle size and higher specific surface area (SSA) than SF. More characteristics of the RHA are given elsewhere [7]. Pozzolanic reactivity of the RHA is comparable with that of the undensified SF [7, 12]. Superplasticizer was a polycarboxylate ether type.

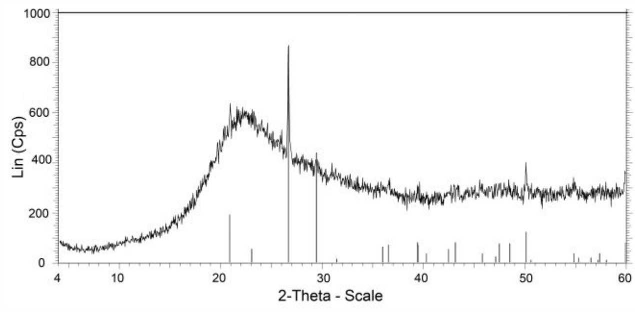

Figure 1. *XRD pattern of RHA*

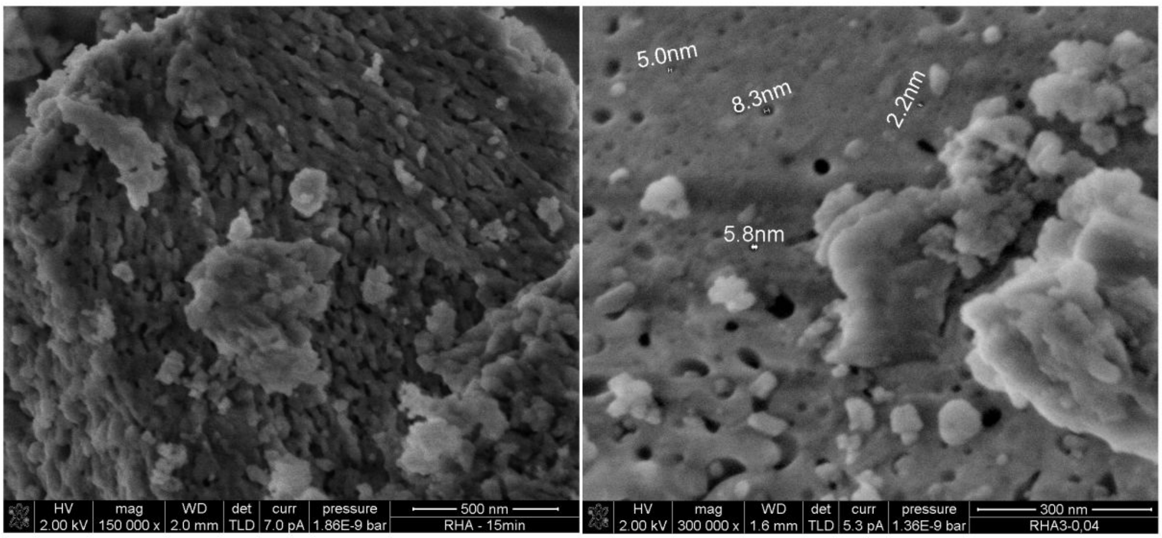

Figure 2. *Surface structure of ground RHA particle*

Table 1. *Chemical composition of cementitious materials, (%)*

	SiO_2	Fe_2O_3	Al_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	L.O.I
Cement	21.6	5.1	3.7	64.3	0.17	0.36	0.6	2.4	0.9
SF	96.0	0.0	0.1	0.6	0.20	0.69	0.2	0.4	1.2
RHA	87.4	0.3	0.4	0.9	0.04	3.39	0.6	0.4	4.6
GGBS	37.8	0.5	8.0	39.7	0.38	0.74	10.8	0.1	0.2

Table 2. *Physical properties of materials*

	Cement	SF	RHA	GGBS	Quartz powder	Quartz sand
Density, (g/cm^3)	3.2	2.3	2.19	2.91	2.64	2.64
Blaine (BET) SSA, (m^2/g)	0.462	(21.05)	(52.3)	0.670	0.438	-
Mean particle size (µm)	9.15	0.31	7.41	2.93	14.6	174.5
Comp. strength of cement (MPa)	3 days:	36.6	7 days:	49.8	28 days:	62.2

2.2 UHPC compositions and testing methods

Based on results of a previous study [10], sustainable UHPC compositions used in this study are given in Table 3. The paste volume is 61 vol.-% of UHPC. Quartz powder is 20 vol.-% of fine materials. W/F_v is volume of water to volume of fine materials ratio. The same volume of RHA and SF is used in mixtures. Pozzolans partially replace cement in volume. Superplasticizer dosage is in dry mass of cementitious materials. 1 vol.-% of steel fibers (a length of 9 mm and a diameter of 0.15 mm) was added to the mixture for producing prisms to determine compressive strength of UHPC. When fibers were used, volume of quartz sand was equally replaced by volume of fibers.

***Table 3.** UHPC compositions*

Mixtures	Cement	Quartz sand	Quartz powder	RHA (SF)	GGBS	Water	SP	W/B	W/F_v
	(kg/m^3)						(wt.%)		
U1-22.5RHA	780.8	1029.6	207.8	155.1	-	216.5	1.0	0.231	0.55
U1-22.5SF				(162.9)				0.229	
U2-22.5RHA	579.3			155.1	183.2		0.8	0.236	
U2-22.5SF				(162.9)				0.234	

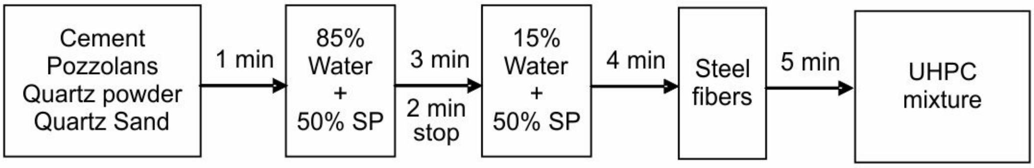

***Figure 3.** Mixing procedure of UHPC*

UHPC was mixed in a Hobart mixer (5 litters) at 140 rpm with a total mixing time of 15 minutes based on the sequence shown in Figure 3. Samples were cast with 30-second vibration and kept in moulds at 20°C, 95% relative humidity (RH) for 48 h followed by 20°C and 100% RH after demoulding until testing. For the durability test, three types of treatment conditions were applied: Treatment 1- 20°C and 100% RH until testing; Treatment 2- 65°C and 100% RH for 48h; Treatment 3- 90°C and 100% RH for 48h. Samples of Treatment 2 and Treatment 3 were stored afterwards at 20°C and 65% RH until testing. To prevent the inhibition of the penetration of water and aggressive agents into specimens, Teflon was used to prepare specimen molds.

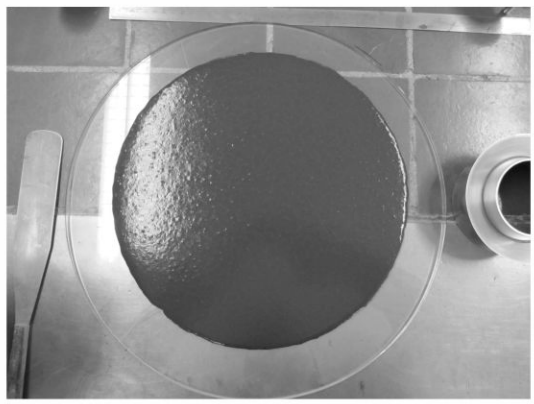

***Figure 4.** Mini-cone slump flow of UHPC*

After mixing, mini-cone slump flow of UHPC mixtures was tested. The mini-cone slump flow values (two diameter values) were measured after further 2 minutes without stroking (Figure 4). Compressive strength of UHPCs was tested on 40 × 40 × 160 mm^3 sized samples in accordance to DIN EN 196-1. Mercury intrusion porosimetry (MIP-Micromeritics, Autopore IV 9500) was conducted on UHPC samples with the pressure up to 230 MPa. The sample was reduced to small grains of 3-5 mm (about 10 g), removed from free water by isopropanol addition and afterwards dried at 40°C until constant weight. Based on the consumed mercury amount during the intrusion process and the respective pressure, the pore size radius distribution between 0.003 to 230 µm and total porosity in UHPC were determined.

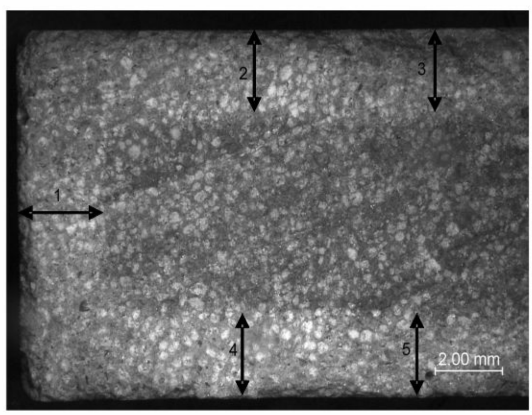

***Figure 5.** Measurement of corrosion depth by phenolphthalein and a digital microscope*

Ammonium nitrate (NH_4NO_3) 5M was used to investigate the deterioration of UHPCs in the aggressive solution. At the age of 28 days under Treatment 1 and 7 days under Treatment 2 and Treatment 3, three and a half UHPC prisms (10 × 40 × 160 mm^3) for each mixture were immersed in the solution at 20°C. The volume of the solution and concrete ratio was 4. The NH_4NO_3 solution was not replaced during the test. The mass change of 3 specimens was measured in dependence of time. Additionally, the corrosion depth of the samples was measured by an acid-base indicator (phenolphthalein) and a digital microscope (VHX 600 II, Keyence). Corrosion depth value is the mean value of five measurements on a 10 × 40 mm cross section sample which was sawed from the half of UHPC bar (Figure 5.).

3. Results and discussion

3.1. Workability and compressive strength

As can be seen from results in Figure 6a, the mini-cone slump flow values of all the UHPCs exceed 270 mm after mixing. When 1 vol.-% of steel fibers is used, it slightly decreases the flowability of the UHPCs. The workability of the RHA-blended mixtures exceeds that of the respective SF-blended mixtures. GGBS clearly improves workability, mixing and casting properties of the UHPC containing RHA or SF.

Compressive strength results of the UHPCs are presented in Figure 6b. At 7 days, compressive strength of U1-22.5RHA exceeds that of U1-22.5SF. Thereafter, the strength of U1-22.5SF and U1-22.5RHA is similar at the ages of 28 and 91 days. Comparing compressive strength of the mixtures containing GGBS (U2-22.5SF and U2-22.5RHA), the strength of the RHA-GGBS-blended UHPC exceeds that of the SF-GGBS-blended UHPC during the first 91 days of hydration. But after even more extended hydration periods (i.e. 180 and 360 days) no significant variation in compressive strength between U2-22.5RHA and U2-22.5SF was observed. Results in Figure 6b also show that the addition of GGBS has a minor influence on compressive strength of the UHPC containing SF. During hydration periods from 28 to 360 days, GGBS clearly enhances the strength of the UHPC containing RHA.

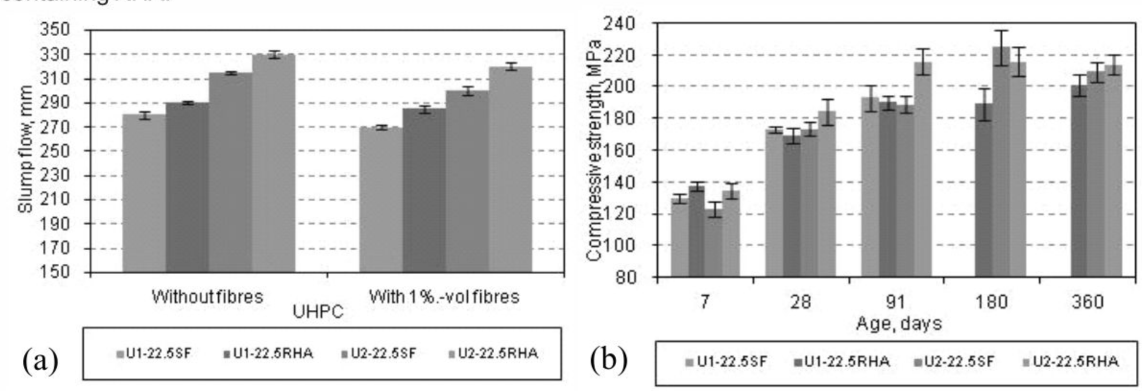

Figure 6. *Workability (a) and compressive strength(b) of UHPC*

3.2. Porosity

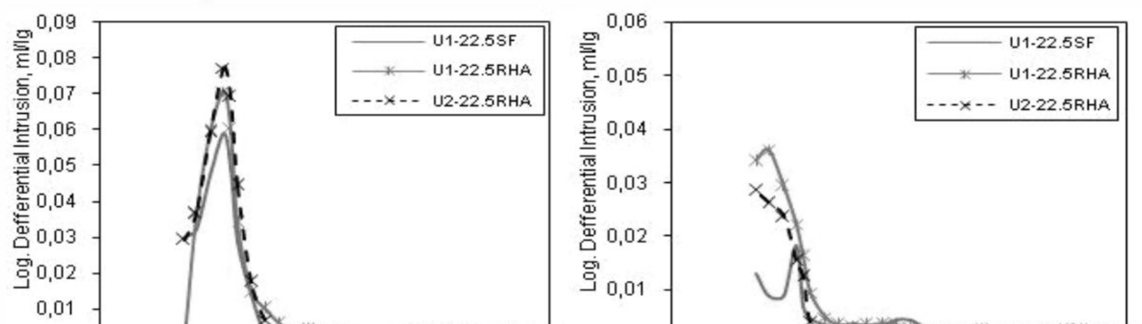

Figure 7. *Pore size distribution of UHPC: a) 7 days; b) 28 days*

Table 4. *Total MIP porosity of UHPC, (%)*

Time of hydration	U1-22.5SF	U1-22.5RHA	U2-22.5RHA
7 days	7.42	7.34	8.30
28 days	4.13	5.43	3.91

The pore size distribution and total porosity of UHPCs measured by MIP are shown in Figure 7 và Table 4. The pore size distribution of the UHPCs at the age of 7 days shows clearly that the critical pore size radius in all the samples is about 0.007 µm. The pore size distribution in U1-22.5SF is better than that in U1-22.5RHA (Figure 7a). However, the total MIP porosity of U1-22.5SF slightly exceeds that of U1-22.5RHA (Table 4). GGBS decreases the density of UHPC containing RHA after 7 days of hydration (Figure 7a and Table 4). With increasing hydration time (28 days, Figure 7b and Table 4), the microstructure of UsHPCs is clearly refined. The refining effect of SF is stronger than that of RHA in the UHPC matrix. The density of the RHA-GGBS-blended UHPC is higher than that of the RHA-blended UHPC and SF-blended UHPC. The density of the UHPCs containing RHA at 28 days even exceeds that of an UHPC containing RHA at w/b of 0.18 investigated by Nguyen Van Tuan [11].

Previous studies indicated that the portlandite (CH) content in a cement paste containing SF is lower or similar to that of a RHA-blended paste at water to binder ratio (w/b) of 0.22 after 7 days of hydration under the normal treatment [7, 11]. The CH content in a cement paste containing RHA is even higher than that in a cement paste containing SF at w/b of 0.18. In the meantime, the cement hydration degree in the matrix containing RHA is lower than in the SF-blended matrix [11]. However, compressive strength (Figure 6b) and density (Table 4) of the UHPCs containing RHA exceeds that of the SF-modified mixtures after 7 days of hydration. It should be noted that the total water content in the mixtures is the same. The specific pore volume of RHA is 0.12 cm^3/g [7] and the content of RHA in the UHPCs is 155.1 kg/m^3 (Table 3). Therefore, the water absorbed by RHA is theoretically about 17.15 l/m^3. Therefore, this leads to a decrease of the effective W/F_v from 0.55 to 0.51 in the mixtures containing RHA. This indicates that the increase in compressive strength and density of the RHA-modified mixtures does not mainly result from the difference in the degree of hydration of cement and pozzolan but from the mesoporous structure of RHA particles (i.e. water absorption). Because puzzolanic reactivity of SF is higher than that of RHA [7, 12], then the pore refinement effect of SF in cement matrix is more significant than that of RHA (Table 4) and hence compressive strength of the SF-modified mixtures is enhanced at the long ages (Figure 6b).

3.3. Durability of UHPCs in NH_4NO_3 solution

Results in Figure 8 and Figure 9 display weight loss and corrosion depth of differently treated UHPCs (20, 65, 90°C) which were exposed to NH_4NO_3 5M up to 12 weeks. The corrosion depth was measured by phenolphthalein and the digital microscopy (Figure 5). Generally, deterioration of the samples develops over time. Corrosion resistance to NH_4NO_3 5M of the SF-modified samples is better than the RHA-modified samples. For UHPCs containing SF, increased corrosion resistance is observed at high temperature of treatment. GGBS slightly improves the corrosion resistance of the UHPC containing SF (Figure 8 and Figure 9). For UHPCs containing RHA, the highest corrosion resistance is obtained for the 65°C treated U1-22.5RHA. The corrosion depth of the 90°C treated U1-22.5RHA is increased compared to that of the 20°C treated sample (Figure 8b). The different treatment conditions do not significantly change the corrosion resistance of the RHA-GGBS-blended UHPC (U2-22.5RHA, Figure 9b). GGBS decreases the weight loss but slightly increases the corrosion depth of all the RHA-modified samples (Figure 8 and Figure 9).

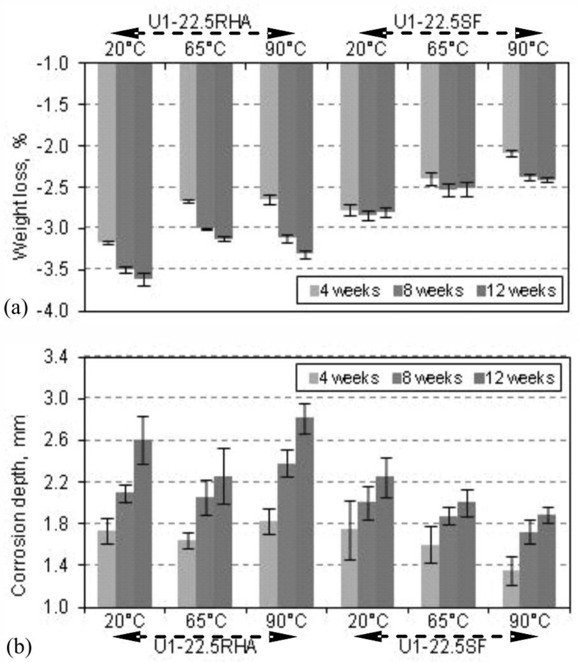

Figure 8. *a) Weight loss and b) corrosion depth of differently treated UHPCs containing RHA or SF in dependence of periods in NH_4NO_3 solution*

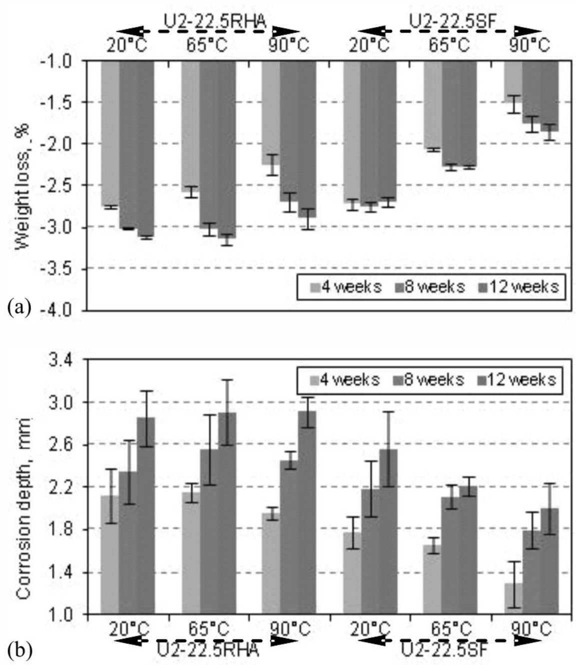

Figure 9. *a) Weight loss and b) corrosion depth of differently treated UHPCs containing GGBS and RHA or SF in dependence of periods in NH_4NO_3 solution*

4. Conclusions

The following conclusions can be drawn from the results of this study:

- With the same water content (i.e. W/F_v = 0.55) and SP dosage, compressive strength of the UHPC containing RHA under the normal treatment is comparable with that of the mixtures containing SF. The incorporation of GGBS and RHA or SF improves workability and compressive strength of UHPC.

- At the age of 7 days, the density of UHPC containing RHA is higher than that of UHPC containing SF. However, the pore refinement effect of SF in the cement matrix is more significant than that of RHA at the age of 28 days. GGBS strongly increases porosity of UHPC containing RHA at the early age but it significanly improves the density of UHPC at the later age.

- The corrosion resistance to NH_4NO_3 5M of the SF-modified specimens is better than the RHA-modified specimens. High temperature of treatment and GGBS slightly improves the corrosion resistance of the UHPC containing SF. Meanwhile, durability of UHPC containing RHA does not significantly change under the different treatment conditions.

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