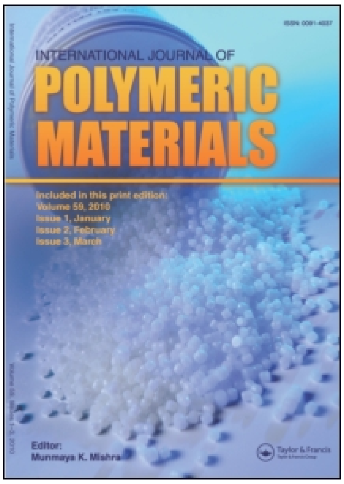


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# Heat Shielding Properties of Water-Containing Plastics

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# Heat Shielding Properties of Water-Containing Plastics

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Water-containing unsaturated polyester (WCP) and fiber reinforced plastics based on it were prepared by an inverted emulsion method and their heat shielding properties were studied by torch burner test at ca. 1500°C and 2500°C. The temperature rise in the resins was considerably retarded with increasing water content for both non-reinforced and reinforced WCP. The retardation of temperature rise due to water was more important at 1500°C than at 2500°C. The weight loss, however, was little affected at 1500°C and increased at 2500°C by the presence of water. The thickness of char layer decreased appreciably with water content. Sucrose dissolved in water had a large effect to retard further the temperature rise and to reduce the rate of weight loss of WCP at 1500°C but the effect was small at 2500°C.

## INTRODUCTION

Water has a high specific heat and a high heat of vaporization. Consequently, when any body capable of transpirating water is heated from its surface, the water can absorb a large quantity of heat through temperature rise and evaporation, and thus bring it out of the body. Furthermore, water vapor over the surface of the body has an effect to reduce the heat input into the surface. This type of cooling is called transpiration cooling and its application for re-entry body has been suggested though its actual use is not yet realized. As is well known, it is the ablation cooling method using plastics that is the most commonly used heat protection method for reentry bodies. If plastics which contain water are heated, it is anticipated that transpiration as well as ablative cooling may be operative.

In our previous paper,[1,2] we have shown that water-containing unsaturated polyster (WCP) can be prepared easily by an inverted emulsion method if



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proper emulsifiers are chosen and some necessary conditions for obtaining stable inverted emulsions are fulfilled. Some preliminary tests for heat protecting properties of WCP have been reported also. For example, when a small plate of WCP (water content: 50 wt.%) of 1 cm thick was heated from one side by a laboratory burner with a flame temperature of ca. 500°C, it did not burn at all for more than 10 min., whereas a test piece of same size made of unsaturated polyester without water began to burn immediately upon being heated. The backside temperature of the test piece of WCP remained unchanged for 7.5 min., whereas that of a test piece made of asbestos mat reached to ca. 240°C in 3.5 min. In another experiment, WCP was heated by an oxy-acetylene torch burner at ca. 2500°C. The temperature rise at the backside was retarded appreciably as compared with unsaturated polyester without water. These results indicated clearly that WCP has high heat shielding or heat protecting properties.

In this work, more detailed experiments are presented to show the characteristics of WCP and fiber reinforced WCP against heat.



## EXPERIMENTAL

### Preparation of WCP

Commercial unsaturated polyester (Ester D32, Mitsuitoatsu Co., Ltd., styrene content: ca. 30%) was used with triethanolamine as an emulsifier. Methyl ethyl ketone peroxide-cobalt naphthenate (MEKPO-CoNh) was used as a curing agent except as otherwise mentioned. Water, in which triethanolamine was previously dissolved, was added gradually to unsaturated polyester prepolymer with vigorous stirring to form a stable inverted emulsion. Then the emulsion was cured for several hours at room temperature followed by post cure for several hours at 40–45°C. The details of the necessary conditions for obtaining stable inverted emulsion are given in the previous paper.[1,2]

### Preparation of Fiber Reinforced WCP

Glass mat was used as reinforcing fibers. The fibers were impregnated with the inverted emulsion mentioned above, hand laid up, cured under pressure for 24 hours at room temperature, then post-cured for several hours at 40–45°C.

### Heat Protection Test

The oxy-acetylene torch burner test at ca. 2500°C has been described already.[2] For the test at ca. 1500°C, propane gas was used in place of acetylene. The flame temperature near 1500°C was measured by an alumel-chromel thermocouple instead of the method using inversion of D line of Na used for 2500°C. The test pieces were 20 mm × 20 mm square and 15 mm thick. In the case of fiber reinforced WCP, the direction of flame was perpendicular to the layer of lamination. An alumel-chromel thermocouple was buried at a desired depth from the backside and fixed by high temperature adhesive. The temperature rise at the location of thermocouple was recorded from the onset of heating which was controlled by a shutter placed between the flame and the test piece. After heating, the weight loss of the test piece was determined. Then the sample was immersed in acryl syrup, fixed by cure, and cut to the heated direction to determine the surface recession and thickness of char layer. When such a precaution was not taken, the surface and char layer were disintegrated into small pieces and powder by cutting.

### Thermogravimetry

Thermogravimetry of WCP and fiber reinforced WCP was carried out in air with a Shimadzu DTA–TGA analyser. Heating rate was 10°C/min.



## RESULTS AND DISCUSSION

### Heat Shielding Effect of Non-reinforced and Reinforced WCP at 1500°C

Figure 1 shows the effect of water on the temperature rise in non-reinforced and glass mat reinforced WCP at 6.4 mm from the original surface heated at ca. 1500°C by a propane-oxygen torch burner. It is obvious that water has an appreciable effect in retarding the temperature rise for both reinforced and

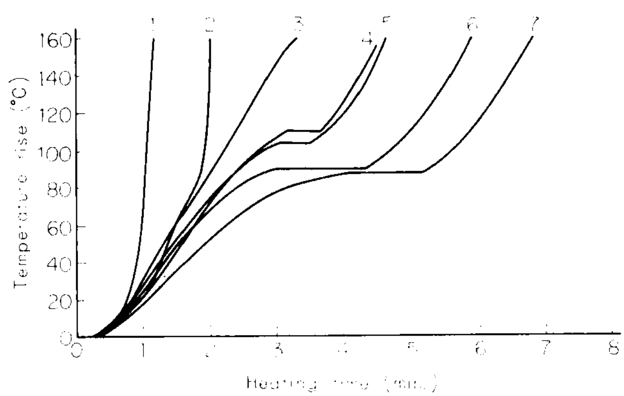


FIGURE 1 Temperature rises in WCP and glass mat reinforced WCP heated at ca. 1500°C. Measured at 6.4 mm from the original surface.
Weight % of components (resin/water/glass mat)
1:(100/0/0), 2:(60/40/0), 3:(60/0/40), 4:(50/10/40), 5:(40/20/40), 6:(30/30/40), 7:(20/40/40).

non-reinforced WCP. Because water has a thermal conductivity one order higher than plastics, the retardation of temperature rise by the presence of water is not a conductive problem but must be due to heat absorption and the transpiration effect of water. In the case of glass mat reinforced WCP, a nearly flat part at about 100°C is seen clearly for each curve. This is apparently due to the evaporation of water. The presence of fibers may make the resin more porous through fiber-resin interface and the transpiration of water more easy.

Similar results were obtained at various positions from the original surface. Using these results, it is easy to construct a figure showing the necessary thickness of WCP for the inside temperature to reach a certain temperature at an arbitrary time. This temperature is set as 150°C in Figure 2. In other words, Figure 2 shows the time necessary for different positions in the test piece to



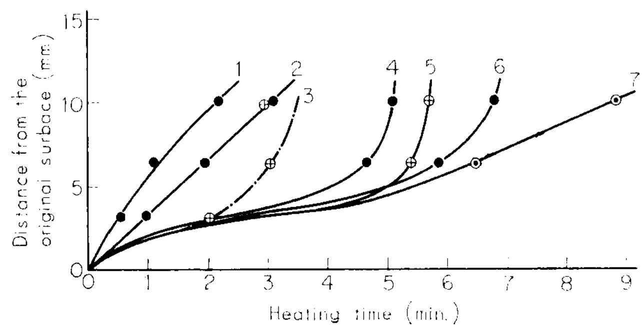


FIGURE 2 Effect of water content on the heat protecting time (time required to reach 150°C) at various positions in WCP and reinforced WCP heated at ca. 1500°C. (The samples are same as in Figure 1.)

reach 150°C. For a same position, the longer the time, the better the heat shielding effect. It is seen from the figure that the heat shielding time increases appreciably with water content. For example, at 1.0 cm from the surface, the time to reach 150°C is retarded by the presence of 40% of water by about 1.5 times for non-reinforced resin and by even 3 times for mat reinforced resin.

Figure 3 shows the weight loss of WCP by heating at 1500°C. The weight loss of non-reinforced WCP is practically identical to that of the original resin. Of course, this does not mean that the ablative phenomena occurring in the non-reinforced WCP and the pure resin are the same. Besides the difference in the temperature distribution in the samples (Figure 1), the water, present in place of resin in WCP, must behave completely differently from the resin in ablation. Water-containing FRP loses weight more rapidly than FRP without water and the weight loss is more pronounced with the increase in water

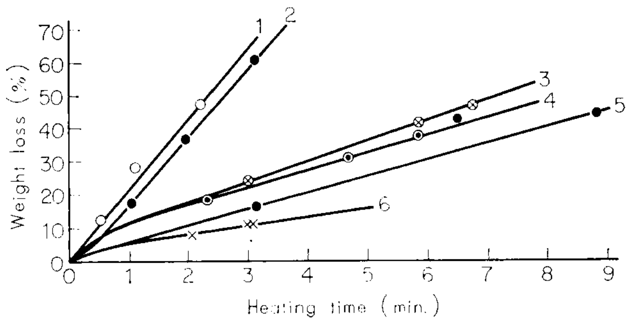


FIGURE 3 Effect of water content on the weight losses of WCP and reinforced WCP heated at ca. 1500°C. (The samples are same as in Figure 1.)

content. This fact, coupled with the results already mentioned concerning the retardation of temperature rise, can be interpreted by the effective transpiration of water in fiber reinforced WCP.

The char layer of glass mat reinforced polyester with water was thinner and more coarse than that of FRP without water. A similar effect will be shown later and discussed in more detail in the case of heating at 2500°C. The glass mats at heated surfaces were melted for FRP without water whereas they remained unchanged for FRP with water. This shows that water vapor keeps the surface temperature lower than the case without water. The resin which has bound fibres was lost gradually from the surface and the char layer remaining became very coarse because the apparent inital resin density is low. As a consequence, the delamination of fibers was often observed after heating.



## Heat Shielding Effect at 2500°C

The temperature rise and weight loss of non-reinforced WCP heated at ca. 2500°C were not very different from those of the resin alone, though they were much faster than those at 1500°C. For example, the rate of ablation (weight loss) of WCP with 40% water was about three times faster than that at 1500°C. Because of higher rate of ablation, the water remote from the heated surface of WCP has not enough time to go out to the surface and does not contribute to retard the temperature rise. Only the resin and water in the surface region are lost as in usual ablation. As stated already, the chemical and physical behavior of water is completely different from that of the resin in ablation. Accordingly the nearly same values obtained for the temperature rise or the weight loss for the WCP and the pure resin are merely the accidental results of the different complex phenomena. In fact, when the pure resin was heated, the burning of gases evolved from the degrading surface was observed. But no combustion was observed for WCP. The surface of WCP after heating was faint yellow and had numerous tiny pores in which the surface is very clean, showing no degradation with charring. Char layer was not formed at all. These facts suggest that abrupt expansion of water droplets near the surface destroy the surface and the char layer.

In our previous paper,[2] we have reported that the WCP cured with benzoyl peroxide at 80°C shows a much slower temperature rise than the pure resin when they are heated at ca. 2500°C. This fact is contrasted with the result of the present work that water has no effect to retard the temperature rise for the WCP prepared by curing with MEKPO-CoNh. The difference may be explained by the different states of the water droplets in these WCP. As has been reported already,[3] the water droplets in the WCP cured with benzoyl peroxide are more continuous than those in the WCP cured with MEKPO-CoNh. Consequently the former may lose water more easily and may have more efficient transpiration effect than the latter in ablative conditions.

Figure 4 shows the effect of water on the temperature rise for the glass mat reinforced WCP heated at 2500°C. In contrast to the non-reinforced resin, the



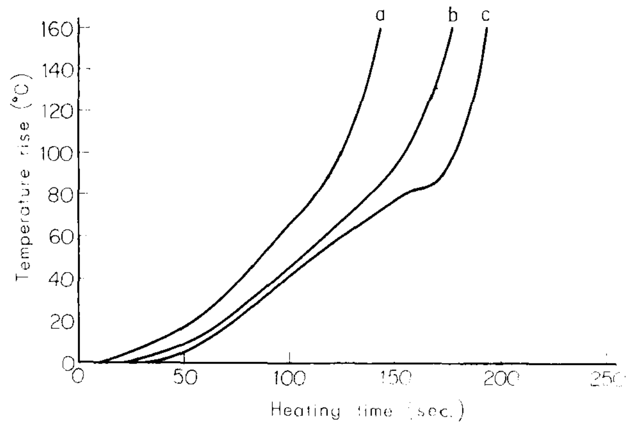


FIGURE 4 Temperature rises in glass mat reinforced WCP heated at ca. 2500°C. Measured at 9.0 mm from the original surface.
Weight % of components (resin/water/glass mat).
a:(50/0/50), b:(40/20/40), c:(20/40/40).

retarding effect of water on the temperature rise is clear. This may be due to the easier transpiration of water through resin-fiber interface as stated in the experiments at 1500°C. Figure 5 shows that the presence of water accelerates the weight loss of mat reinforced WCP. The accelerating effect is stronger at 2500°C than at 1500°C. The effect of water on the surface recession and char layer thickness is given in Figure 6. It is clearly seen that the rate of surface recession increases and the thickness of char layer decreases with the

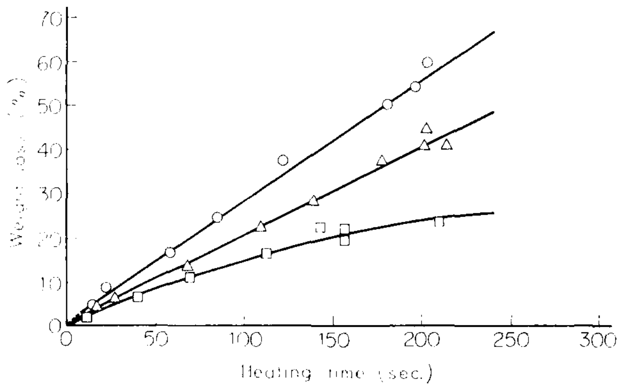


FIGURE 5 Weight losses of glass mat reinforced WCP heated at ca. 2500°C. □:(50/0/50), △:(50/10/40), ○:(20/40/40).

water content. Figure 6 shows also that a quasi steady state of ablation is reached earlier for higher water content.

These results may be interpreted as follows. At 2500°C, where the heat input is very large, the fraction of heat absorbed by water must be small as compared with that at 1500°C. Consequently, the effect of water to retard the temperature rise is smaller at 2500°C than at 1500°C. The water vapor over the surface may block somewhat the heat input and the surface temperature in the presence of water may be lower than that in the absence of water. But these effects are not very large because of the large heat input at 2500°C. On the other hand, the presence of water contributes to weaken the mechanical strength of the surface and the char layer. When water is evaporated, the remaining FRP has many voids and the char layer after the thermal degradation of the resin is very coarse. When this char layer grows to a certain thickness, it may be destroyed by the force of the flame. The abrupt expansion of water may also contribute to the disintegration of the char layer. This is the reason for the thinner char layer and higher rate of ablation with higher water content. The thinner char layer may also contribute to increase the rate of ablation because the heat input to the interface between the char layer and the degrading resin will increase.

## Thermogravimetry of WCP and Reinforced WCP

The mode of heating in a thermobalance is completely different from that by a torch burner. In a thermobalance, a sample is heated uniformly and the temperature is in equilibrium throughout the sample. Accordingly, the thermal conductivity and the heat absorption due to specific heat and vaporization may have no effect on the thermogram, As a consequence, if there is no chemical

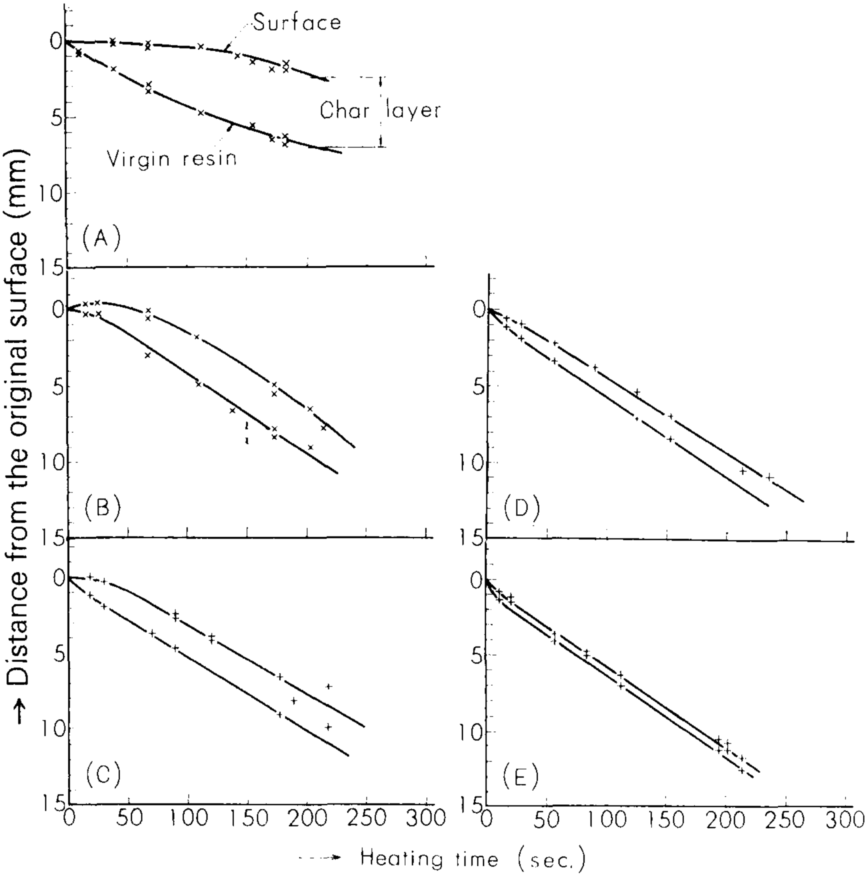


FIGURE 6 Surface recession and char layer thickness of reinforced WCP heated at ca. 2500°C.
Weight % of components (resin/water/glass mat)
(A):(50/0/40), (B):(50/10/40), (C):(40/20/40), (D):(30/30/40), (E):(20/40/40).

interaction between water and unsaturated polyester by heating, the thermogram must be a superposition of the loss of weight by vaporization of water and that by chemical degradation of the resin itself. This is the case as is shown in Figure 7. At about 100°C, the most of water contained is lost in both WCP and reinforced WCP. Then at near 350°C, where the resin without water is decomposed rapidly, the non-reinforced and reinforced WCP loose weight just in the same manner as the original resin. These results show that the chemical reaction of polyester with water must be negligible in such a condition and that

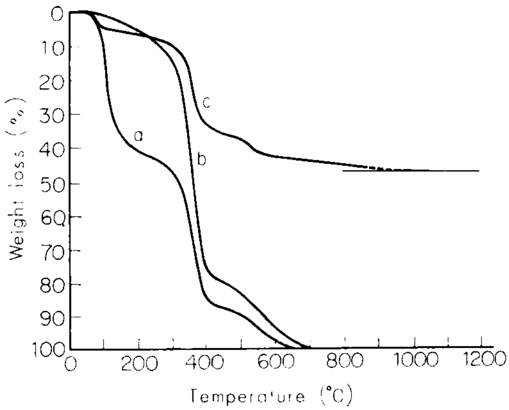


FIGURE 7 Thermogravimetric curves of WCP and reinforced WCP.
Weight % of components (resin/water/glass mat)
a :(60/40/0), b :(100/0/0), c :(40/10/50).
Heating rate: 10°C/min., in air.



water droplets are continuous enough to permit the almost complete vaporization of water when heated slowly.

## Effect of Sucrose on the Thermal Properties of WCP

Sucrose is known to be carbonized easily by heat to produce water and carbon ($C_{12}H_{22}O_{11} \rightarrow 12C + 11\ H_2O$). Water will serve as a transpirating agent and carbon will be useful to thicken the char layer which resists the weight loss. Furthermore, the presence of sucrose may depress the vapor pressure of water and retard its vaporization. These are the reasons why sucrose is chosen as as an additive. Figure 8 shows a thermogravimetric curve of WCP with sucrose.

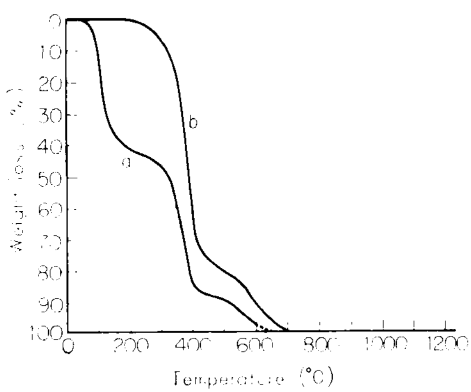


FIGURE 8 Effect of sucrose on the weight loss of WCP in thermogravimetric analysis.
Weight % of components (resin/water/sugar).
a :(60/40/0), b :(40/40/20).

The effect of the addition of sucrose is remarkable. Water is not lost at 100°C but it is kept up to about the decomposition temperature of the resin. We are not sure that the retardation of vaporization is entirely due to the vapor pressure depression. It might be also possible that water droplets in WCP prepared in the presence of sucrose is less continuous. The fact that water is less volatile in WCP with sucrose was confirmed also by a breathing experiment; i.e., when WCP prepared with sucrose was kept in dry air, it lost water far more slowly than WCP without sucrose.

The temperature rise and weight loss of WCP with sucrose heated at 1500°C are compared with WCP without sucrose in Figures 9 and 10. The effect of



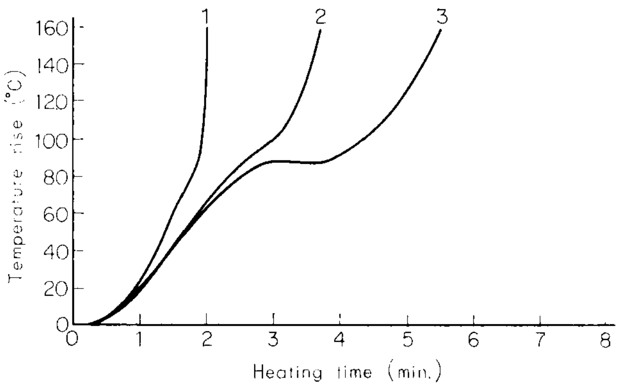


FIGURE 9 Effect of sucrose on the temperature rise of WCP heated at ca. 1500°C. Measured at 6.4 mm from the original surface.
Weight % of components (resin/water/sucrose/glass mat).
1:(60/40/0/0), 2:(40/40/20/0), 3:(20/20/10/50).

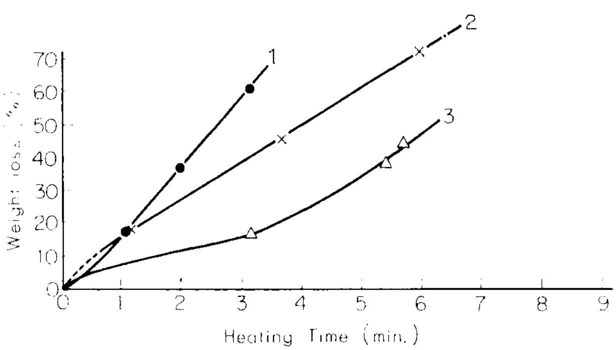


FIGURE 10 Effect of sucrose on the weight loss of WCP heated at ca. 1500°C. (The samples are same as in Figure 9.)

sucrose is obvious. The temperature rise is retarded and the weight loss reduced. But at 2500°C, the difference between the temperature rise of WCP with and without sucrose is not very large and the weight losses of the two materials were nearly identical. The same reasoning as that for the lower effect of water at 2500°C than at 1500°C on the heat shielding properties of WCP may be applied also to the effect of sucrose.

## CONCLUSION

WCP has higher heat shielding properties than the original resin without water. The effect of water to retard the temperature rise is more important at lower temperature. The weight losses are little affected or rather increased by the presence of water. Sucrose dissolved in water increases the heat shielding effect of water, especially at low temperature. The effect of water seems to be dependent on the state of water droplets in WCP. This must be elaborated further.

### Acknowledgement

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