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Pre-treatment of calcium-based paper ash for cement admixture application

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The paper industry in Korea has continued to grow at a high pace. The annual amount of paper sludge generated during the wastewater treatment process in the paper manufacturing process is about 1.6 million tons. In addition, paper sludge is recycled as paper ash after incineration, but most of it is landfilled. Therefore, this study aimed to use calcium based paper ash as cement admixture generated in the production process of neutral paper-making process to have various uses of paper ash. In order to use paper ash as a cement admixture, pre-treatments such as pre-hydration and hydration control are required. As a result, the characteristics of paper ash and the formation of ettringite were found to be good when 12% of hydration water and 10% of anhydrous gypsum were mixed. Also, it was shown that when pre-treated paper ash with a less than 10% of OPC was used as a cement admixture, good compressive strength and workability could be obtained. Especially, cement mixed with pretreated paper ash showed excellent shrinkage resistance performance compared to OPC.

Key words: Paper ash, Cement admixture, Prehydration, Hydrate control, Waste recycling.

Introduction

The domestic paper industry is the fifth largest producer of paper and paperboard in the world and has continued to grow at a high rate until now. [1] The paper manufacturing process uses cellulosic fiber, which is a woody resource, as its main raw material and produces products by adding various organic and inorganic additives. In addition, the paper manufacturing process can be divided into paper-making process, finishing process and wastewater treatment process, and various solid wastes are generated in each unit process.

The wastes generated in the wastewater treatment process of solid waste are referred to as paper sludge and in the past, it was common to be treated by landfill, marine dumping, etc. [2] However, in accordance with the revision of the Enforcement Regulations of the Waste Management Act, landfilling of paper sludge has been prohibited since 2003 and in accordance with the 2006 London Convention on the Prohibition of Industrial Dumping of Marine Wastes, marine dumping of wastes in 2012 was totally banned. Therefore, paper sludge is currently treated by the heat treatment method such as incineration to prevent the corruption by organic matter and soil pollution of landfill. [3] In addition, domestic paper sludge generation is about 1.6 million tons per year and paper ash generated after incineration of paper sludge is reported to be used in various fields such as compost, solidifying agent, soil for gardening, fuel and so on. However, the recycling rate of paper ash is about 20% so that it is a situation that most of it is landfilled. [4]

In the paper-making process, inorganic filler is added to improve the optical and physical properties of the paper. Generally, the most commonly used fillers include calcium carbonate, talc, titanium dioxide, and clay. In addition, major components of paper ash produced when incinerating paper sludge can be divided into calcium type paper ash and silica type paper ash depending on the type of inorganic filler.

In this study, calcium-based paper ash was tried to be used as cement admixture to increase recycling rate of recycled paper ash. In order to use calcium-based paper ash as a cement admixture, a pretreatment plan should be made. Pre-hydration through water addition and control of hydrates by mixing gypsum were used as pretreatment methods for paper ash. Also, the physical properties of pretreated paper ash mixed cement were examined by measuring the compressive strength, flow and rate of change after preparing mortar specimens mixed with pretreated paper ash.

Experimental Method

In this study, paper ash was used as cement admixture. In order to use paper ash as a cement admixture, analysis of calcium-based paper ash characteristics, optimization of pre-hydration condition, optimization of hydrates and examination of pretreated paper ash mixed mortar properties were carried out.

Regarding the method for analyzing paper ash

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characteristics, calcium-based paper ash produced during the production of neutral paper-making was obtained and then chemical composition analysis was implemented for it by using an inductively coupled plasma spectrometer (ICP-OES 8300, Perkin Elmer, USA). Also, the crystal phase analysis of paper ash was performed by using an X-ray diffractometer (XRD, D/MAX-3000, Rigaku, JAPAN).

Hydration water was mixed to optimize prehydration condition of paper ash after analysis of chemical composition and crystal phase. The amount of hydrated water was controlled to 5%, 8%, 12% and 16% of the weight of paper ash and mixed at the condition of 500 rpm-30 minutes in a ball mill. The hydration characteristics of the paper ash crystals were analyzed for the paper ash mixed with hydration water by using an X-ray diffractometer. Next, gypsum was mixed to optimize hydrates of paper ash. The hydrate was prepared and analyzed after the mixing ratio (5%, 10% and 15%) and type (anhydrite, hemihydrate, dihydrate) of the gypsum were controlled and mixed with paper ash. The water/binder ratio(w/b) was fixed to 40% and the manufactured paste was cured in water bath until each curing time (3 days, 7 days) after a day at 23 °C-90%RH. Analysis of hydrates and microstructure observation were performed for thy hydrate which finished its curing per its curing period by using X-ray diffractometer, scanning electron microscope (SEM, SM300, Topcon, JAPAN) and thermogravimetric analyzer (DTG-60H, Shimadzu, JAPAN), and gypsum type and optimum condition of mixing ratio was derived.

The pretreated paper ash in the above process was mixed with 5%, 10%, and 15% ratios of cements to prepare the mortar specimens and physical properties were examined. When manufacturing mortar specimens, water/binder ratio (w/b) and sand/binder ratio (s/b) was fixed to 62% and 250% and mortar flow, compressive strength and length change rate were examined.

Result and Discussion

Analysis of calcium-based paper ash

In order to analyze the physicochemical properties of calcium-based paper ash, the paper ash from A company in Korea was obtained. As shown in Table 1, the main compositions of paper ash were CaO, SiO_2, Al_2O_3 and Fe_2O_3, Na_2O, SO_3, etc. exist as minor components. CaO content was 54.2% and SiO_2 content was 15.8%. In particular, ignition loss was 12.2%, which is due to decarboxylation of limestone and pyrolysis of organic fibers. [5] Fig. 1 shows separation of the organic fibers in paper ash. Generally, paper sludge is burned in an incinerator at 800 ~ 900 °C for about 2 ~ 3 seconds and due to the short sludge retention time, some of the untreated cellulose fibers remain in the paper ash. When the paper ash is used for a certain amount or more, the workability of the mortar or concrete will be lowered by the fibers above.

As shown in Fig. 2, the main crystal phases of paper ash were $CaCO_3$, CaO and $C_{12}A_7$ ($12CaO \cdot 7Al_2O_3$). Besides, peaks of quartz and $Ca(OH)_2$ were also detected. The peak of $Ca(OH)_2$ which is detected as a small amount is considered to be the hydrate formed by the reaction of CaO present in the paper ash with moisture in the atmosphere.

The CaO and $C_{12}A_7$ react with the mixed water to rapid-setting and $CaCO_3$ is a substance which has little hydration reaction. [6] Therefore, CaO and $C_{12}A_7$ should be controlled so as not to cause rapid-setting and deterioration of physical properties in the process of applying mortar or concrete by the pre-hydration, when applying paper ash.

Derivation of optimum condition for prehydration

In order to control the rapid-setting of paper ash, the hydration characteristics of CaO and $C_{12}A_7$ crystals were observed by changing the hydration water content to 5%, 8%, 12% and 16% of the paper ash. Fig. 3 shows the XRD pattern for each hydration water content and $Ca(OH)_2$ and C-A-H (CaO-Al_2O_3-H_2O) were detected as major hydrates. It was observed that while the peak intensity (Intensity, CPS (counts per

Table 1. Main chemical composition of calcium-based paper ash.
[unit: wt%]

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	LOI
15.8	9.29	1.22	54.2	3.42	0.89	0.27	0.72	12.2

(a) Paper ash (b) Fiber

Fig. 1. Example of paper ash and fiber.

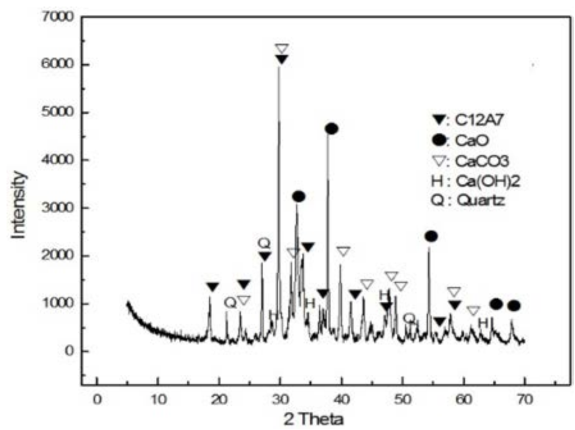


Fig. 2. XRD pattern of paper ash.

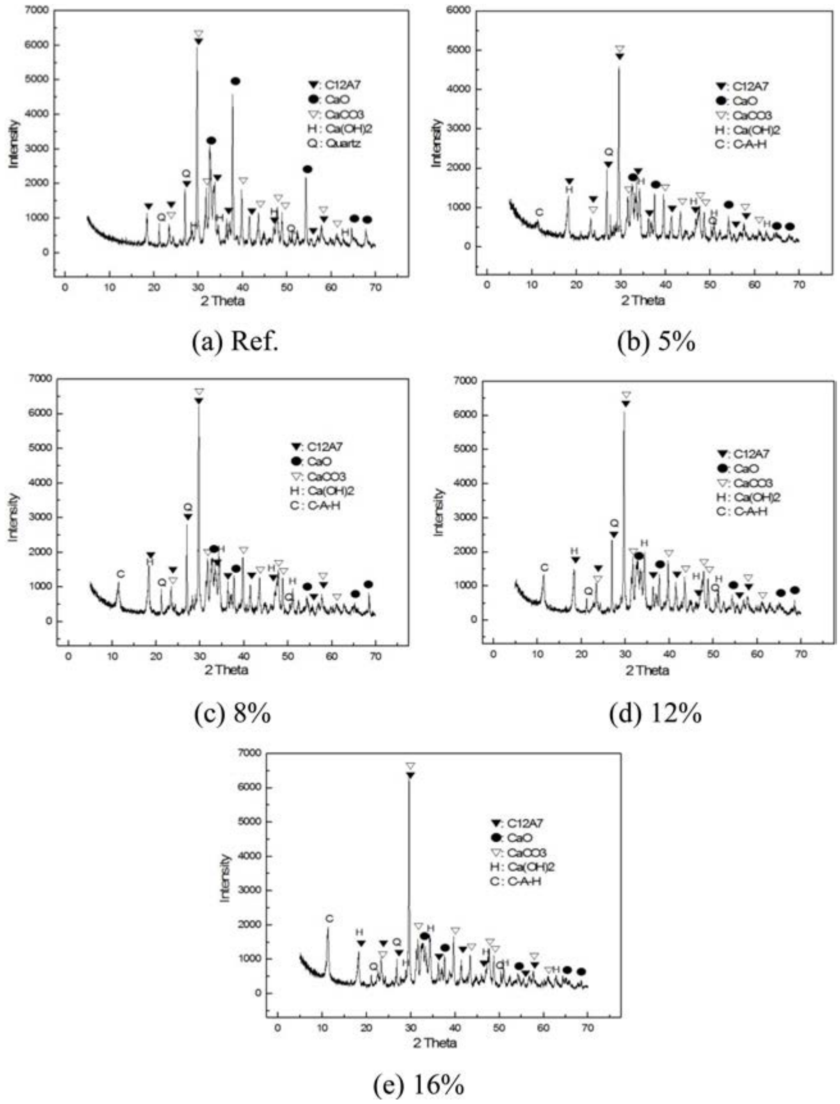
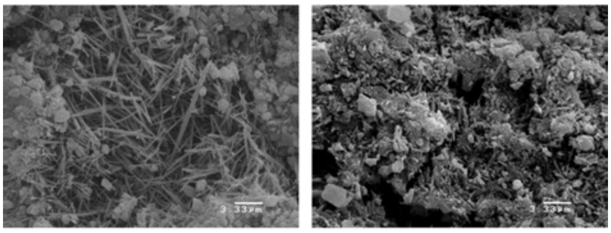


Fig. 3. XRD pattern of paper ash by hydration water's mixing ratio.

second)) of $Ca(OH)_2$ near 34 ° was detected to be very small even in (a) Ref. pattern where hydrated water is not added, the peak intensity became bigger as the hydration water contents increased. However, the peak strength was not improved any more at 12% or higher. In addition, it was confirmed that the C-A-H peak intensity near 11 ° also steadily increased with increasing hydration water. On the contrary, the peaks of CaO and $C_{12}A_7$ tended to decrease significantly with increasing hydration water. The drawback that the aggregation phenomenon of the paper ash (a phenomenon in which the particles are clumped and by a large amount of hydration water) is generated under the condition of 16% hydration was derived. However, there is no aggregation up to 12% of hydration water so that 12% was considered appropriate for the optimum hydration yield for paper ash pretreatment.

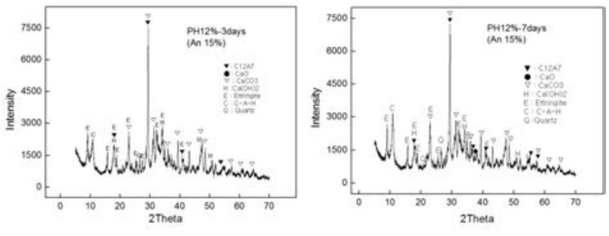
Optimization of hydrates

Among the paper ash crystalline phases, $C_{12}A_7$ reacts with mixed water to produce C-A-H crystals. Although the C-A-H crystal is a representative hydrate that is generated rapidly during the initial hydration process, it is known that the strength-expressing function is different depending on the ratio of each component consisting of C-A-H. [7] CA ($CaO \cdot Al_2O_3$) is superior in strength, but C_3A and $C_{12}A_7$ are known to be poorer than CA. Therefore, the C-A-H crystal must be changed, and a method of reacting with the gypsum among the methods for crystal change can be mentioned. [8] That is, the C-A-H crystal is reacted with the gypsum to induce the production of ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$). Ettringite is one of representative cement hydrates and it is also a method to introduce initial strength enhancement. Therefore, this study also investigated if the formation of ettringite is present after making hydrates of paper ash



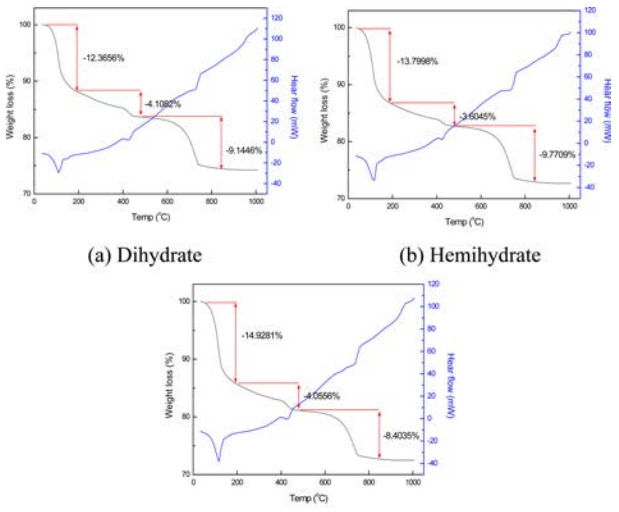
(a) 3days (b) 7days

Fig. 4. Microstructure of paper ash hydrate mixed with anhydrous gypsum.



(a) 3days (b) 7days

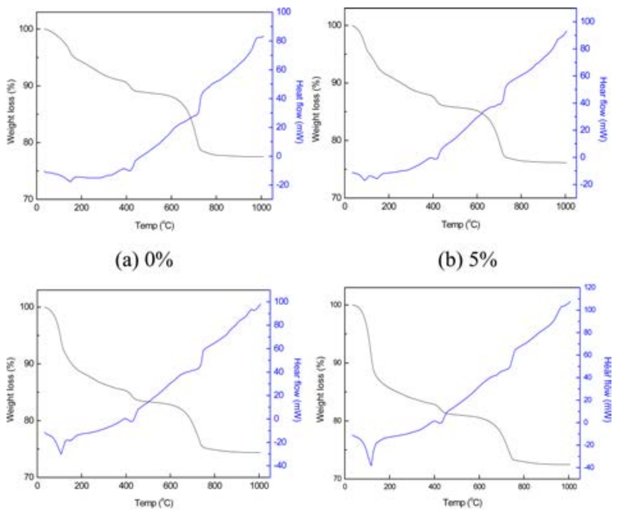
Fig. 5. XRD pattern of paper ash hydrate mixed with anhydrous gypsum by curing time.



(a) Dihydrate (b) Hemihydrate

(c) Anhydrite

Fig. 6. TG-DSC curve of 3days cured paper ash paste by gypsum type.



(a) 0% (b) 5%

(c) 10% (d) 15%

Fig. 7. TG-DSC curve of 3 days cured paper ash paste by anhydrous gypsum mixing ratio.

and gypsum mixtures. Fig. 3 shows microstructure photograph of paper ash hydrate where 15% anhydrous gypsum is mixed with respect to cement for different curing periods. In the microstructure photograph of paper ash hydrate with different curing periods, ettringite which is acicular hydrate can be observed and it was found that the amount of ettringite increases with increasing curing period. In other words, it was confirmed that paper ash was able to hydrate with anhydrous gypsum and was able to produce ettringite sufficiently. Figure 5 shows the XRD patterns of paper ash hydrates by anhydrous gypsum content and curing period and it can be seen that the peak intensity of ettringite near 9 ^{o} increases as the anhydrous gypsum content increases. It was also found that the amount of ettringite increased with the increase of curing period.

In order to select the optimum type of gypsum suitable for calcium-based paper ash (anhydrite, hemihydrate, dihydrate), the hydrates by gypsum type were prepared and then went through thermal analysis. Generally, ettringite, $Ca(OH)_2$ and $CaCO_3$ have endothermic peaks near 110 ºC, 460 ºC and 750 ºC respectively. [9] Fig. 6 shows 3 days of curing TG-DSC curve on the paper ash hydrate mixed with various 15% gypsums with respect to cement. The result of thermal analysis has shown that the weight loss values of the ettringite peaks in mixed hydrates such as anhydrite, hemihydrates, dihydrate were -12.4%, -13.8% and -14.9%, respectively. In other words, when anhydrous gypsum is mixed with paper ash, the production of ettringite would be the best.

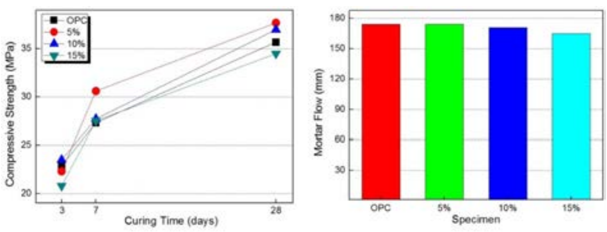
For optimization of anhydrous gypsum's mixing ratio, paper ash-anhydrous gypsum paste were prepared and went through thermal analysis after the mixing ratio was controlled to 5%, 10% and 15% with respect to paper ash. Fig. 7 shows 3 days of curing TG-DSC curve on the hydrate by anhydrous gypsum mixture ratio. Thermal analysis result of paper ash hydrate with no added anhydrous gypsum has shown that an endothermic peak of CAH appears at 150 ºC. An endothermic peak of $Ca(OH)_2$ is observed at around 450 ºC and an endothermic peak due to decarbonation reaction ($CaCO_3 \rightarrow CaO + CO_2$) of limestone appears at around 750 ºC. In the case of hydrates mixed with 5% and 10% of anhydrous gypsum, an additional endothermic peak was observed at around 100 ºC. It is believed that this is caused by the formation of ettringite due to the mixing of anhydrous gypsum. Also, the CAH peak near 150 ºC gradually decreases from 10% substitution of anhydrous gypsum and at 15% substitution condition, only ettringite peak is observed.

Therefore, in order to convert all of CAH into ettringite, it is considered that anhydrous gypsum of 10% or more with respect to paper ash should be substituted.

Review of physical properties of mortar mixed with pre-treated paper ash

Mortar flow and compressive strength were measured to investigate the physical properties of cement mixed with pretreated paper ash. Also, the length change rate of mortar was measured to evaluate dry shrinkage reduction performance of mortar with increasing amount of ettringite.

As shown in Fig. 8(a), the compressive strength of OPC was 22.9 MPa on 3 days, 27.3 MPa on 7 days, and 35.7 MPa on 28 days. In pre-treated paper ash mixed cement, there was no specific trend according to paper ash content. However, the compressive strength was higher than that of OPC at 5 ~ 10% of paper ash mixing condition, but the compression strength was 91% of OPC at 15% mixing condition. Fig. 8(b) shows the mortar flow of cement mixed with pretreated paper ash, and the flow of OPC was 174 mm. Mortar flow decreased slightly as the pretreatment paper ash content increases. Especially, the mortar flow was 165 mm at the mixing condition of 15% pretreated paper ash and it was 95% of OPC. However, the flow is 97 ~ 100% when mixing with 5% and 10% of pretreated paper ash so that it showed results similar with OPC flow.



(a) Compressive strength (b) Flow

Fig. 8. Physical properties of mortar mixed with pretreated paper ash.

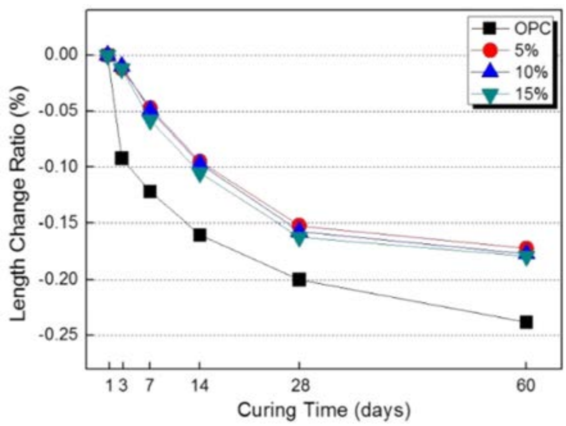


Fig. 9. Length change rate of mortar mixed with pretreated paper ash by curing time.

Generally, to reduce dry shrinkage of mortar, quicklime or gypsum based materials are mixed to use. This is because the CaO component reacts with the mixed water to produce $Ca(OH)_2$ so that volume expansion occurs. In addition, the process in which the calcium aluminate component and the gypsum react with each other to form ettringite is also accompanied by volume expansion. [10] Therefore, the stability of pretreated paper ash mixed cement was also examined by measuring the dry shrinkage resistance characteristic of the paper ash mixed cement which is the length change rate of the mortar.

Fig. 9 shows the percent change in length of mortar mixed with pretreated paper ash by curing time. Length change rate's measurement result shows that the shrinkage rate increased with increasing curing time in all mortar specimens. Also, the shrinkage rate was highest in OPC mortar and mixing pretreated paper ash has a better shrinkage percentage compared to OPC. It was considered that the hydration reaction of pretreated paper ash produced more ettringite so that it affected shrinkage reduction.

Considering the compressive strength, mortar flow and length change rate above, the use amount of 10% is considered to be suitable if pretreated paper ash is used.

Conclusions

This study aimed to use calcium based paper ash as cement admixture which is generated in the manufacturing process of neutral paper-making. In order to use paper ash as a cement admixture, calcium-based paper ash characteristics were analyzed and optimum conditions of pre-hydration and optimum condition for hydrates were derived. In addition, after pretreatment paper ash was mixed with cement to produce mortar, the characteristics were analyzed and the following conclusions were drawn.

1) The main crystal phase of calcium-based paper ash consists of $CaCO_3$, CaO and $C_{12}A_7$ and since CaO and $C_{12}A_7$ react rapidly with water, it is necessary to use pretreatment process for cement admixture.

2) The crystal phase analysis result of paper ash with hydration water mixing has shown that the $Ca(OH)_2$ and C-A-H peak intensities increased as the hydration water content increased while the peaks of CaO and $C_{12}A_7$ decreased drastically. However, at 16% of hydration water, part of paper ash was formed into 1 ~ 2 mm of particles and it reduces workability so that it was found that hydration water content should be mixed to 12% level.

3) To obtain good compressive strength during the paper ash hydration reaction, C-A-H crystals were reacted with gypsum to produce ettringite crystals. Microstructure observation and crystal phase analysis of paper ash hydrates by gypsum type and mixing ratio

have shown that the production of ettringite was observed. And, the thermal analysis result of paper ash paste mixed with gypsum has shown that the best ettringite formation was seen at 10% anhydrous gypsum of mixing condition.

4) The compressive strength analysis result of mortar mixed with pretreated paper ash has shown that compressive strength value similar to or higher than OPC was obtained in 5 to 10% paper ash of mixing condition. Also, the mortar flow value was similar to that of OPC at less than 10% of paper ash. Also, it was confirmed that the length change rate of mortar shows excellent shrinkage resistance compared to OPC according to pretreated paper ash mixing.

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