中國環境工程學刊 第十卷 第四期 (民國八十九年)
Journal of the Chinese Institute of Environmental Engineering, Vol. 10, No. 4, pp. 261-270 (2000)

ENHANCEMENT OF POZZOLANIC ACTIVITY AND MORPHOLOGY OF SEWAGE SLUDGE ASH BY CALCINATION

Dyi-Hwa Tseng and Shi-Cheng Pan

Graduate Institute of Environmental Engineering
National Central University
Chungli, Taiwan, R.O.C.

Chau Lee

Department of Civil Engineering
National Central University
Chungli, Taiwan, R.O.C.

Key Words : Sewage sludge ash, mortar, pozzolanic activity, calcination, fly ash

ABSTRACT

The feasibility of using sewage sludge ash (SSA) in mortar to replace partial cement has been proved by many researches. However, the irregular morphology and low pozzolanic activity limit the utilization of SSA in mortar. This research used a calcination process followed by water quenching to modify SSA. The modified ash produced from this process is named calcined sewage sludge ash (CSSA). According to the study results, the CSSA calcined at 1,000℃ to 1,200℃ has higher pozzolanic activity than raw SSA due to higher content of amorphous silicon oxide. Besides, due to partial or full melting of SSA when calcined at high temperature, the surface of CSSA particle becomes smoother and less porous. In this study the CSSA calcined at 1,200℃ was used in mortar to replace cement at different levels. The results indicate that, for different levels of cement replacement at constant w/c ratio, CSSA obviously has better performance on workability and strength development than raw SSA. Compared with fly ash, CSSA calcined at 1,200℃ has almost equal performance to fly ash. According to the results from this study, the high-temperature calcination followed by water quenching is confirmed to be an effective process to improve the surface properties and pozzolanic activity of SSA.

INTRODUCTION

The sewage sludge ash (SSA) is a residue produced from sewage sludge incineration facilities. Many research works have been devoted to developing a beneficial utilization of SSA [1,2,3,4,5]. Among those different technologies, using SSA as pozzolan in mortar or concrete has been studied and confirmed to be technically and economically feasible. However, two major disadvantages were found when using SSA in mortar. First, many researchers have found that the compressive strength of mortar decreased with the increasing use of SSA [1,6]. This is due to the lower pozzolanic activity of SSA than common pozzolans such as fly ash. Tay and Show [1] have evaluated the pozzolanic activity of SSA by strength activity index. The research results showed that the strength activity index of SSA is about 58% ~ 67%. These values are lower than 124% ~ 134% of fly ash. Tseng *et al*. [7] have found that the strength activity index of SSA is about 54% ~ 74%, which is also lower than 96% ~ 98% of fly ash. The lower pozzolanic activity of SSA directly affects the strength development of SSA mortar. Second, many researchers have found that the water demand of SSA mortar is higher than common cement mortar [4,8,9]. This is due to the irregular morphology and water-adsorption capacity of ash particles. In this situation, at least one undesired condition will happen. In other words, the w/c ratio must be raised otherwise the workability of mortar will be reduced.

The disadvantages of SSA must be modified before being utilized in mortar or concrete. Some researchers have found that the calcination process can successfully improve the pozzolanic activity of materials [10,11]. Calcination at high temperature can transfer some crystalline silicate or aluminate into amorphous form. Besides, the partial or full melting of SSA at high temperature may also change its morphology. For these reasons, this study was conducted to establish the feasibility of modifying SSA by calcination treatment. The process used in this study included the calcination of SSA, followed by water quenching. The calcination process is expected to solve two problems of SSA at the same time. The pozzolanic activity and other performances in mortar containing calcined SSA were compared with raw SSA and fly ash in this study.

METHODS AND MATERIALS

1. Sewage Sludge and Ash

The sewage sludge used in this study was sampled from Ming-Shen Community Wastewater Treatment Plant (MSCWWTP), Taipei City. MSCWWTP is a typical sewage treatment plant with secondary biological processes. As shown in Fig. 1, the sampled sludge was incinerated and the raw SSA was ground into fine particles. Part of the raw SSA was calcined, water-quenched, and then ground. The product was named calcined sewage sludge ash (CSSA). The temperatures of calcination were controlled at 700, 800, 900, 1,000, 1,100, and 1,200℃.

The physical and chemical properties of SSA and CSSA were analyzed. The properties of fly ash obtained from Lin-Ko Power Plant were also analyzed for the purpose of comparison. Table 1 summarizes the major chemical composition of raw SSA and fly ash. The physical properties of SSA, CSSA, and fly ash were summarized on Table 2. The analyzed physical properties included specific gravity, Blaine's fineness, and specific surface area. Besides the physical and chemical analysis, the morphology of SSA, CSSA, and fly ash was also determined by a scanning electron microscopy (SEM).

Table 1. Chemical compositions of SSA and fly ash

Composition (%)	SSA	Fly ash
SiO_2	41.3~56.1	41.8
Al_2O_3	14.7~16.5	17.0
Fe_2O_3	8.2~8.5	5.3
CaO	2.1~5.3	5.9
P_2O_5	1.7~1.9	0.46
MgO	1.7~2.3	1.6
SO_3	1.5~1.7	0.72
Na_2O	0.23~0.31	0.23
K_2O	1.9~2.0	0.56

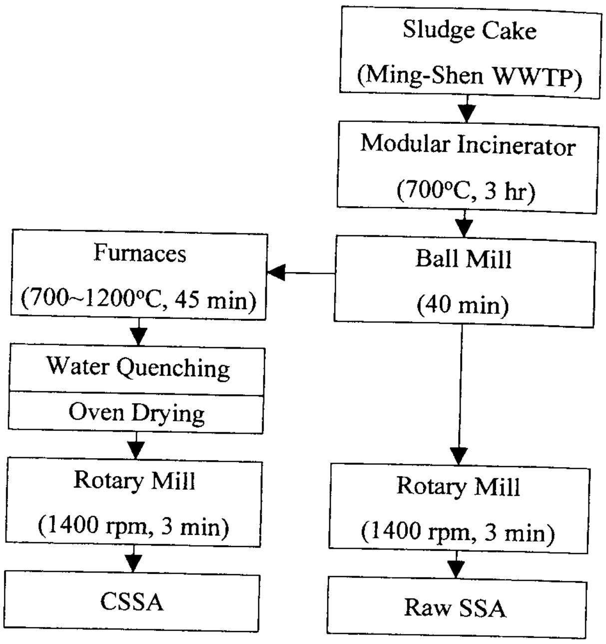

Fig. 1. The preparation procedures of raw SSA and CSSA.

Table 2. Physical properties of SSA, CSSA, and fly ash

Material	Specific gravity	Blaine's fineness (m^2/kg)	Specific surface area (m^2/kg)*
SSA	2.61	1,578	4,705
CSSA			
700℃	2.63	1,589	6,029
800℃	2.66	1,575	4,907
900℃	2.65	1,310	648
1,000℃	2.64	580	323
1,100℃	2.56	392	151
1,200℃	2.61	370	154
Fly ash	2.61	512	985

* BET specific surface area was tested by nitrogen adsorption method.

2. Pozzolanic Activity and Reaction

According to ASTM C311, the pozzolanic activity of pozzolans can be represented by strength activity index (SAI). The SAI of SSA, CSSA, and fly ash were evaluated in this research. Corresponded lime pastes were also prepared in order to examine the hydration product of pozzolanic reaction. The crystalline of raw ashes and hydration products were identified by X-ray diffractometry (XRD).

3. Cement Mortar

The batching, mixing, and curing of cement mortar in this study was according to ASTM

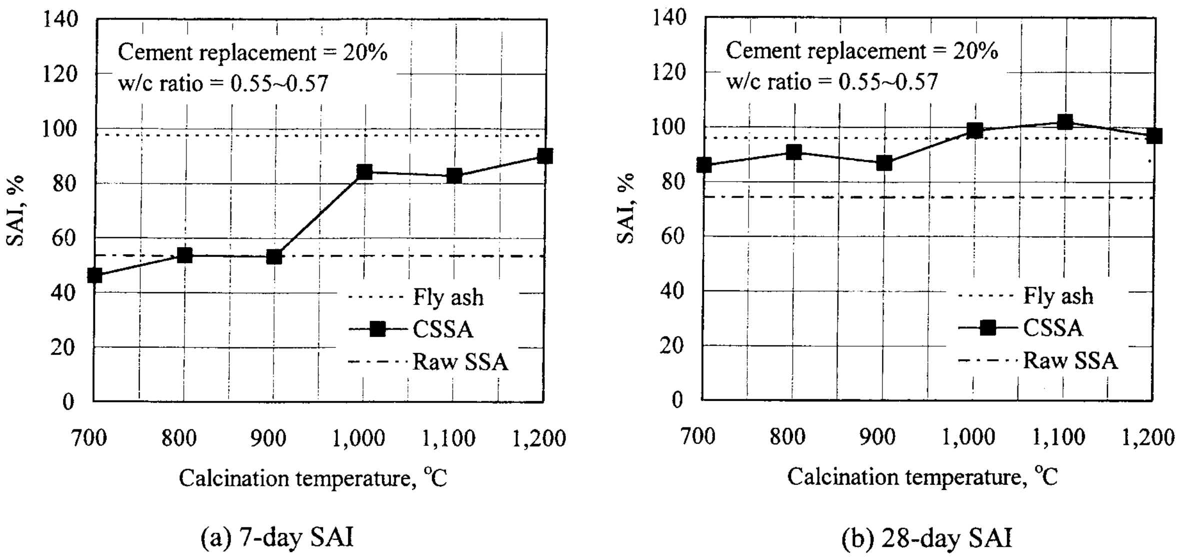

Fig. 2. The pozzolanic activity of SSA, CSSA, and fly ash.

C109. The 5 cm (2-inch) cubic mortar samples were prepared at constant water-to-cement (w/c) ratio. The SSA and CSSA calcined at 1, 200℃ were selected to replace mortar cement. The cement replacement was designated at 5%, 10%, 20%, 30%, and 50%. For comparison, the fly ash mortar and control mortar were also prepared.

4. Workability and Strength Development

According to ASTM C109 and ASTM C230, the workability of fresh mortar was evaluated by flow table spread (FTS). The strength of hardened mortar was evaluated by its compressive strength according to ASTM C109. The compressive strength of mortar was observed on 1, 3, 7, 14, 28, and 180-day of curing age.

RESULTS AND DISCUSSION

1. Pozzolanic Activity of CSSA

As shown in Fig. 2, the raw SSA has low pozzolanic activity. The SAI of raw SSA is about 54%~74%. The 7-day SAI of raw SSA was also found much lower than 28-day SAI. It implies that the reactivity of raw SSA is low. In contrast, the fly ash was found to have high pozzolanic activity either regarding 7-day SAI or 28-day SAI. The SAI of fly ash was about 96%~98%. Figure 2 also shows the SAI of CSSA calcined at different temperatures. According to this diagram, the enhancement effect on pozzolanic activity varies with calcination temperature. In the low-temperature range (700~900℃), the 7-day SAI of CSSA is as low as that of raw SSA. However, the 28-day SAI of CSSA is higher than that of raw SSA. In the high-temperature range (1,000~1,200℃), both 7-day and 28-day SAI of CSSA is higher than that of raw SSA. As shown in Fig. 2, the SAI of CSSA calcined at low and high temperatures are 46%~91% and 83%~102%, respectively. The low-temperature calcination enhances only 28-day SAI. The highest value of SAI is still lower than that of fly ash. In contrast, the high-temperature calcination can improve both 7-day SAI and 28-day SAI to similar level of that of fly ash.

The phenomenon of pozzoalnic activity enhancement of SSA by calcination can be investigated through XRD. Figure 3 shows the XRD data of fly ash, raw SSA, and CSSA. The relative content of any species identified can be represented by its highest X-ray intensity in the spectra. According to that, the raw SSA has highest content of crystalline silicon oxide, which major form is identified as quartz. In contrast, the fly ash was found to have lowest content of crystalline silicon oxide. The CSSA calcined at low temperature was found to have similar content of crystalline silicon oxide to that of raw SSA. However, the content of crystalline silicon oxide of CSSA significantly decreased when calcination temperature raised to 1,000~1,200℃. The reduced content of crystalline silicon oxide can be explained as the result of partial or full melting of SSA, since some researchers have reported that the vitrification temperature of SSA is about 1,060 ~ 1,120℃ [12,13]. As described in the following formula, the crystalline silicon oxide will transform into amorphous form by high-temperature calcination and water quenching:

$$\text{S (crystalline)} \rightarrow \text{S (amorphous)} \quad (1)$$

The notation S in above equation represents

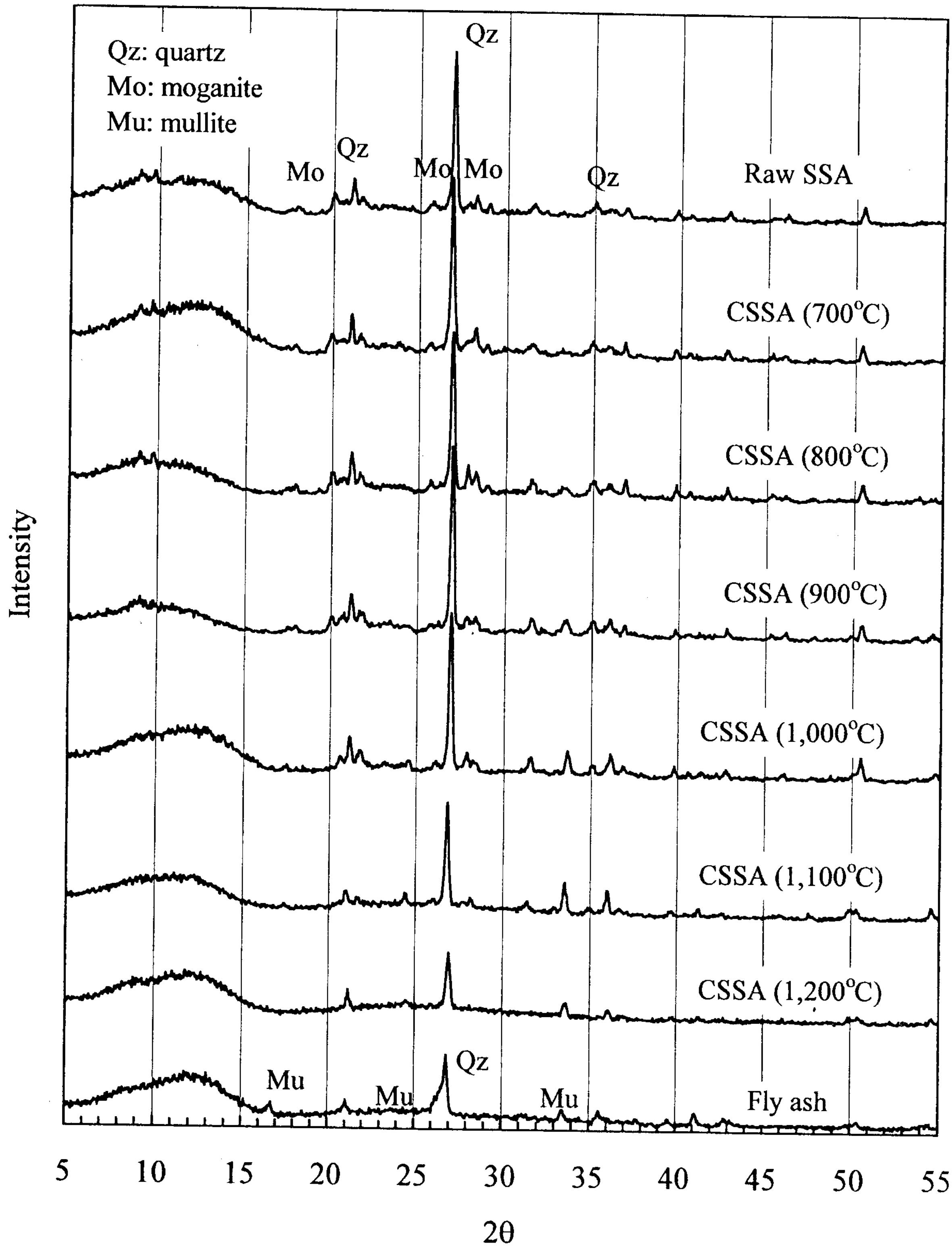

Fig. 3. The XRD results of SSA, fly ash, and CSSA.

silicon oxide. In pozzolanic reaction, only amorphous silicon oxide was reactive. In contrast, the crystalline silicon oxide was inert. According to following equation of pozzolanic reaction, the calcium silicate hydrate (C-S-H) will be produced through hydration of amorphous silicon oxide, calcium hydroxide (CH), and water (H):

$$CH + S\ (\text{amorphous}) + H \rightarrow C\text{-}S\text{-}H \qquad (2)$$

In order to verify the pozzolanic reaction and

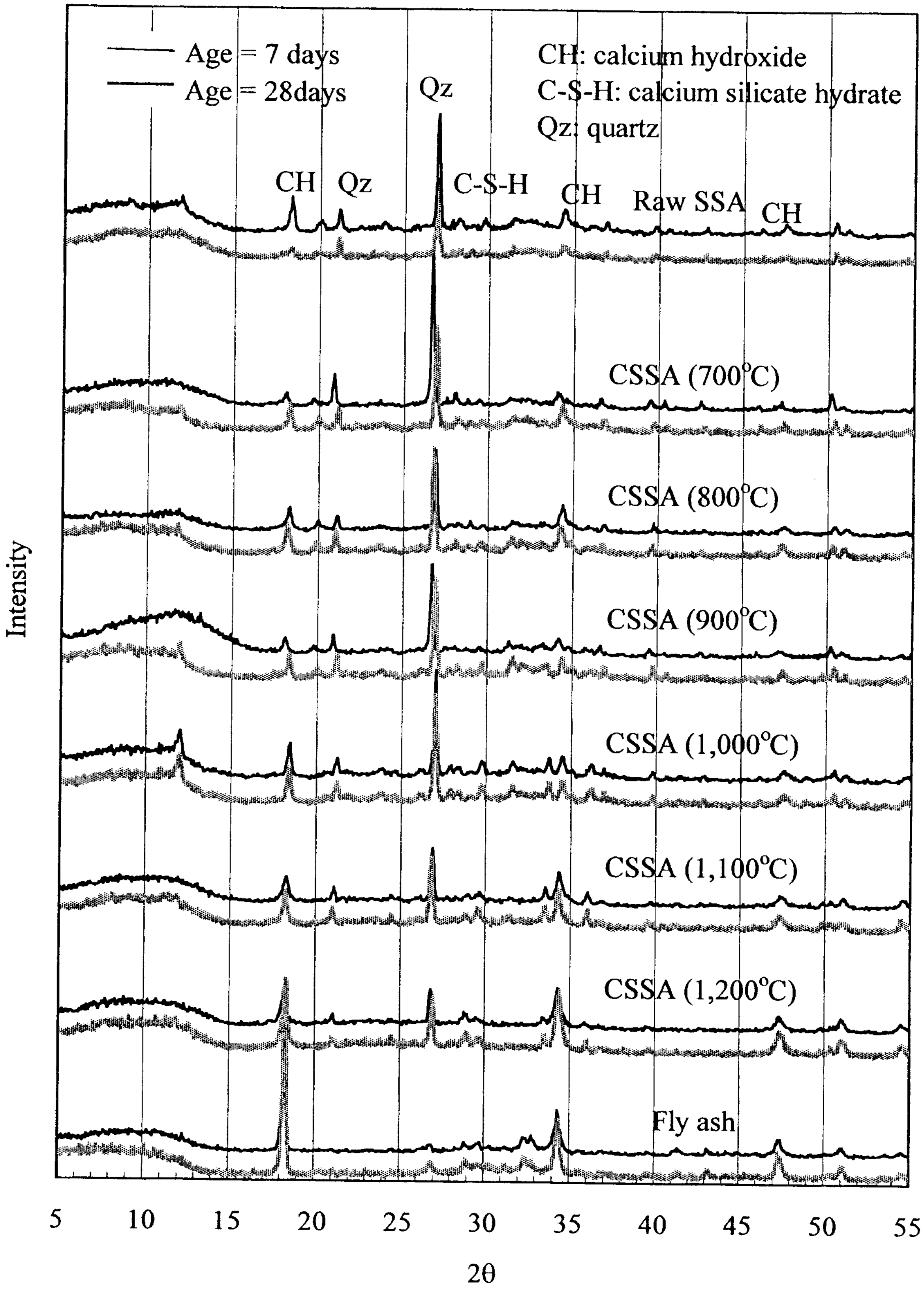

Fig.4. The XRD results of SSA, fly ash, and CSSA lime pastes.

its hydration product, the lime pastes containing raw SSA, fly ash, and CSSA were prepared, cured, and analyzed by XRD. Figure 4 shows that the C-S-H gels are found in each lime pastes at dif-

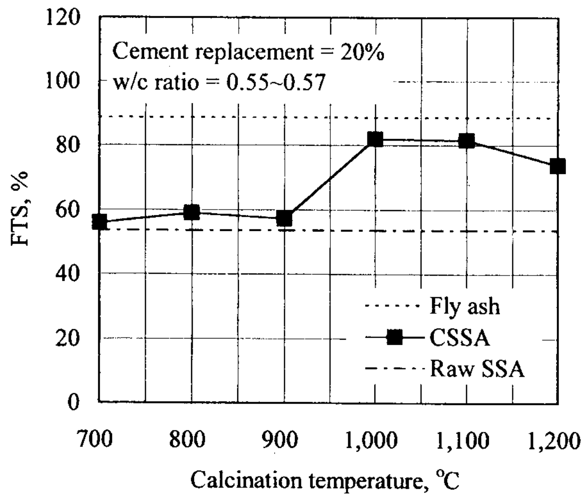

Fig. 5. The workability of control mortar and ash-amended mortars.

ferent curing ages. The C-S-H gels produced from pozzolanic reaction were similar to that from portland cement hydration. Both of them could provide compressive strength to mortar. According to that, the fly ash, in which content of amorphous silicon oxide is higher than that of raw SSA, will produce more C-S-H gels when used in mortar. Consequently, the SAI of fly ash mortar is higher than raw SSA mortar. On the other hand, the high-temperature calcination significantly reduced the content of crystalline silicon oxide and increased the content of amorphous silicon oxide. The SAI of CSSA (calcined at high temperature) mortar was equal to that of fly ash mortar. Similarly, its pozzolanic activity is obviously higher than raw SSA. According to that, the enhancement effect of high-temperature calcination on pozzolanic activity of SSA is established.

2. Workability of CSSA Mortar

As shown in Fig. 5, the FTS of raw SSA mortar is as low as 54%. In contrast, the FTS of fly ash mortar is as high as 89%. These results confirmed the finding of the adverse effect of SSA on mortar workability reported by many researchers [4,8,9]. The effect of CSSA on mortar workability improvement was also examined. Also, as shown in Fig. 5, the FTS of mortar containing CSSA calcined at low temperature is as low as that of raw SSA mortar. In contrast, the workability of mortar containing CSSA calcined at high temperature was obviously improved. Its performance is similar to that of fly ash mortar.

The phenomenon of workability improvement of mortar containing high-temperature calcined CSSA was investigated by the morphology observation of ash particles. The study and discussion of morphology in this study were based on the SEM images of ash particles. As shown in Fig. 6a, the morphology of raw SSA is very irregular and porous. In contrast, as shown in Fig. 6h, the fly ash particles are spherical grains. The surface of fly ash particle was smooth and no pores are observed. As mentioned previously, the irregular surface of SSA would increase the internal friction of fresh mortar. In the mean time, the greater surface area of SSA would adsorb more mixing water. These two effects together could reduce the workability of SSA mortar. As shown in Fig. 6b~d, the low-temperature calcination has no obviously effect on improving the morphology of SSA. The morphology of CSSA calcined at low temperature is as irregular and porous as that of raw SSA. This can explain why there was almost no workability improvement observed after using low-temperature calcined CSSA in mortar. On the other hand, as shown in Fig. 6e~g, the particle surface of CSSA becomes smoother and less porous when calcination temperature was raised to 1,000~1,200℃. The fact of this phenomenon is resulted from partial or full melting of SSA during calcination. For this reason, the mortar containing CSSA calcined at high temperature has similar high FTS as that of fly ash mortar.

Another experiment was carried out to confirm the enhanced effect of high-temperature calcination on SSA morphology. As shown in Fig. 7, the effect of CSSA (calcined at 1,200℃) and fly ash on mortar workability was compared at different cement replacement levels. Like the fly ash does, the CSSA (calcined at 1,200℃) mortar could maintain almost equal FTS at different levels of cement replacement. In contrast, the workability of raw SSA mortar decreased when the cement replacement ratio raised. According to above findings, the enhancement effect of high-temperature calcination on the surface morphology of SSA is confirmed.

3. Strength Development of CSSA Mortar

In order to obtain further confirmation on the performance of CSSA calcined at high temperature, the CSSA calcined at 1,200℃ was selected for further investigation. The CSSA calcined at 1,200℃ was applied into mortar to replace cement at different levels. The strength development of raw SSA mortar, CSSA mortar, and fly ash mortar are summarized in Fig. 8 and 9 and 10, respectively. As the hydration of cement and pozzolans were in process, the compressive strength of hardened mortar increased with the increasing of curing age. For raw SSA mortar at certain curing age, the compressive strength decreased with the increasing of cement replacement. This implies that the content of amorphous silicon oxide is in-

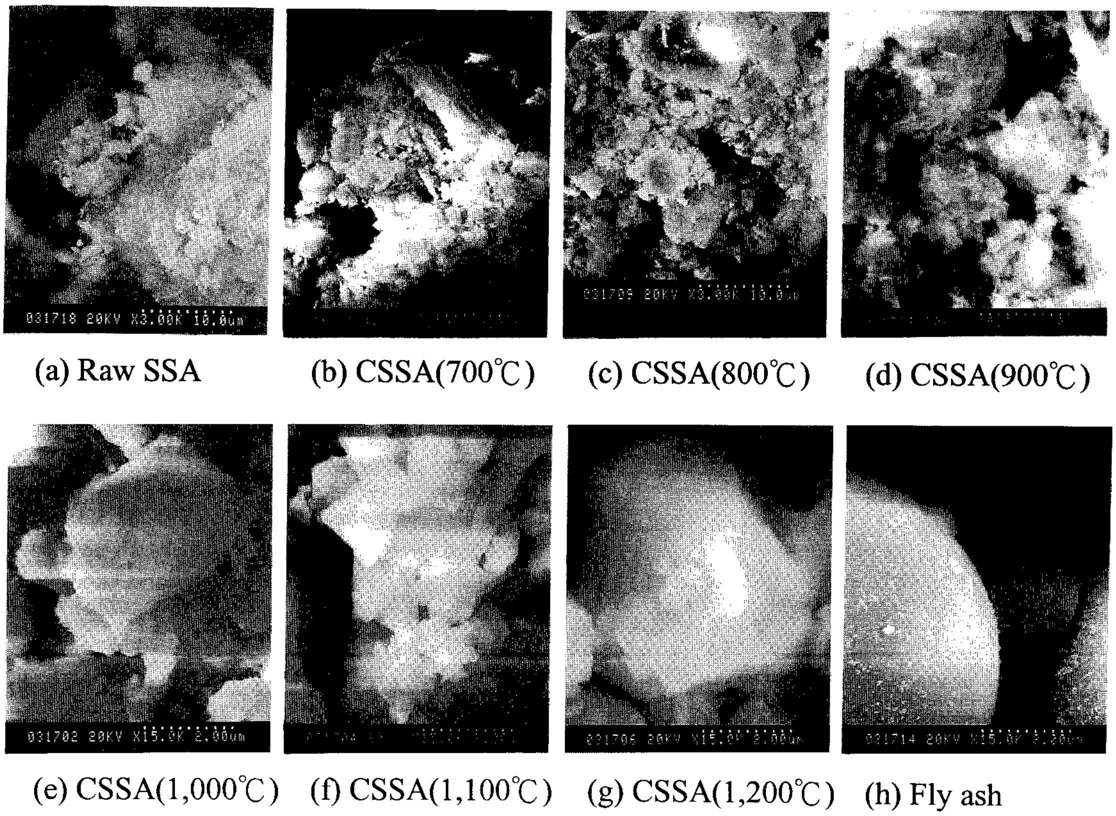

Fig.6. The SEM images of raw SSA, CSSA, and fly ash.

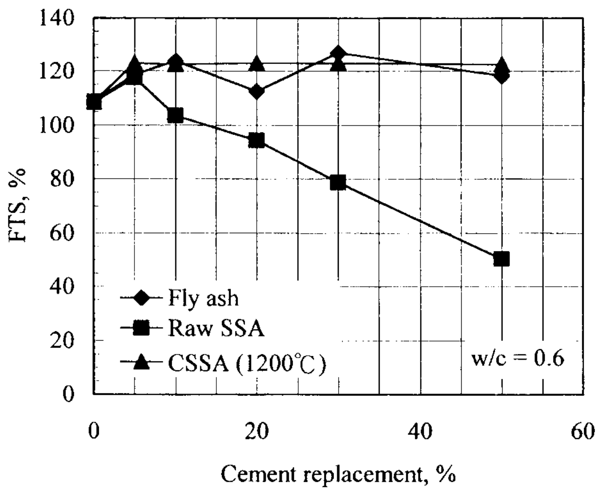

Fig.7. The workability of SSA, CSSA, and fly ash mortars.

sufficient to produce necessary volume of C-S-H gels. Comparing Fig. 8 and 9, the performance of CSSA calcined at 1,200℃ is found obviously better than raw SSA. Accordingly, the calcination process performed in this study is confirmed to be successful on enhancing SSA again.

As shown in Fig. 10, the fly ash mortar, in which cement replacement is below 20% has higher compressive strength than the control mortar at age 180-day. The mechanism, by which the later strength gain is obtained, is the reduction of capillary pore volume [14]. The capillary pores of hardened paste were filled by continuously produced C-S-H gel from pozzoalnic reaction. Meanwhile the continuous consumption of calcium hydroxide also helped mortar to improve its strength. On the other hand, in Fig. 9, the CSSA calcined at 1,200℃ shows a similar performance to that of fly ash at all replacement ratios before the 28-day of curing age. However, the compressive strength of CSSA mortar is lower than the control mortar at age 180-day for all replacement levels. There are two possible reasons to explain this phenomenon. First, the content of amorphous silicon oxide of CSSA calcined at 1,200℃ is lower than that of fly ash. The content of amorphous silicon oxide of CSSA would be sufficient for its hydration with calcium hydroxide at early ages. However, the remaining amorphous silicon oxide becomes insufficient for further hydration at later ages. Second, as the pozzolanic reaction was in process, the amorphous silicon oxide of CSSA becomes non-reactive. Consequently, no more C-S-H gels are produced at later ages. Because the data from this study are not sufficient enough to verify the hypothesis of this phenomenon, further investigation will be carried out in the future.

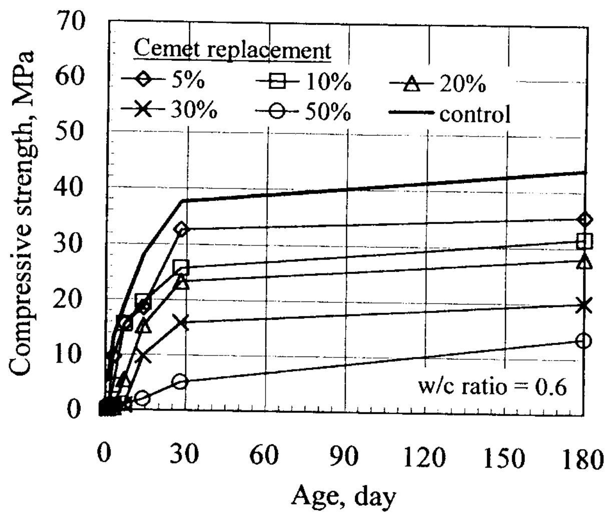

Fig. 8. The strength development of raw SSA mortars at different cement replacement.

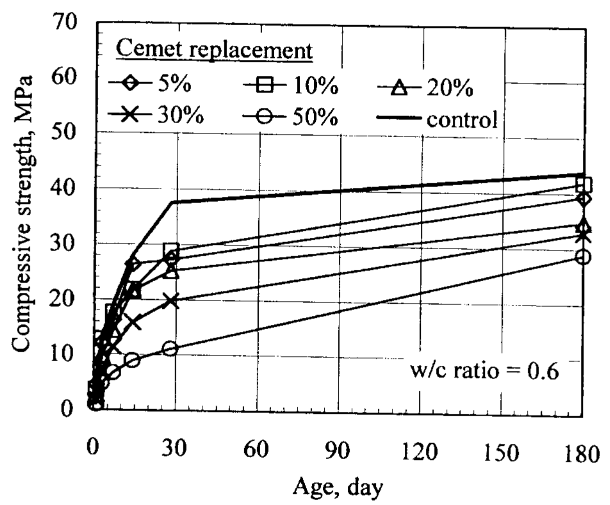

Fig. 9. The strength development of CSSA (calcined at 1,200℃) mortars at different cement replacement.

CONCLUSIONS

According to the research results of this study, the CSSA calcined at high temperatures (1,000~1,200℃) obviously has higher pozzolanic activity than raw SSA. This is resulted from the increased content of amorphous silicon oxide of CSSA. The workability of CSSA mortar is also improved due to smoother and less porous morphology of ash particles. When using CSSA (calcined at 1,200℃) in mortar to replace cement, it has similar performance on workability and early strength development as that of fly ash. Accordingly, the high-temperature calcination process followed by water quenching can be established to be an effective modification process for SSA. However, the CSSA (calcined at 1,200℃) mortar was also found having lower compressive strength than that of fly ash mortar at later ages. This mechanism and necessary modification of this phenomenon needs further investigation.

AKNOWNLEDGEMENTS

This research was granted by National Science Council, Republic of China (project number: NSC 88-2211-E008-030). This article presents only part of the research results of this project.

REFERENCES

1. Tay, J. H., and K. Y. Show, "The Use of Lime-Blended Sludge for Production of Cementitious Material," *Water Environ. Res.*, 64(1), 6-12 (1992).
2. Tay, J. H., and K. Y. Show, "Reuse of Wastewater Sludge in Manufacturing Non-Conventional Construction Materials - an Innovative Approach to Ultimate Sludge Disposal," *Water Sci. Technol.*, 26(5-6), 1165-1174 (1992).
3. Hiraoka, M., "Advanced Sludge Thermal Processes in Japan," *Water Sci. Technol.*, 30(8), 139-148 (1994).
4. Monzo, J., J. Paya, M. V. Borrachero, and A. Corcoles, "Use of Sewage sludse Ash (SSA) - Cement Admixtures in Mortars," *Cement and Concrete Res.*, 26(9), 1389-1398 (1996).
5. Tay, J. H., "Bricks Manufactured from Sludge," *ASCE J. Environ. Eng.*, 113(2), 278-284 (1987).
6. Tay, J. H., "Sludge Ash as Filler for Portland Cement Concrete," *ASCE J. Environ. Eng.*, 113(2), 345-351 (1987).
7. Tseng, D. H., S. C. Pan, and C. Lee, "The Properties of Sewage Sludge Ash and Its Application in Cement Mortar," *Proc. 9th Sewerage Technol. Conf.*, pp. 239-253 (1999).
8. Bhatty, J. I., and K. J. Reid, "Compressive Strength of Municipal Sludge Ash Mortars," *ACI Materials J.*, 86(4), 394-400 (1989).
9. Tay, J. H., W. K. Yip, and K. Y. Show, "Clay-Blended Sludge as Lightweight Aggregate Concrete Material," *ASCE J. Environ. Eng.*, 117(6), 834-844 (1991).
10. Salvador, S., "Pozzolanic Properties of Flash-Calcined Kaolinite: A Comparative

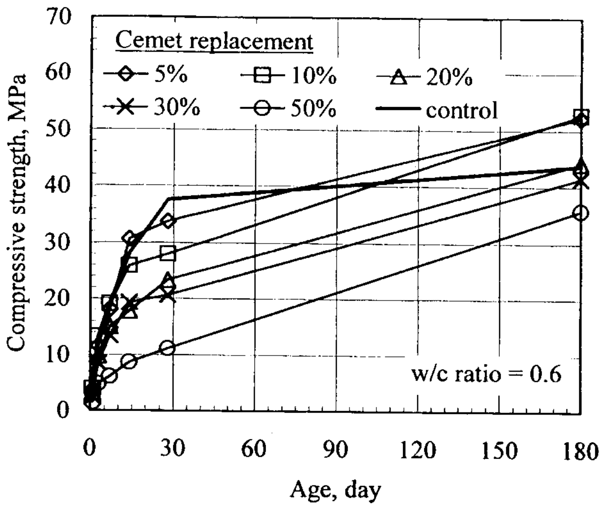

Fig. 10. The strength development of fly ash mortars at different cement.

Study with Soak-Calcined Products," *Cement and Concrete Res.*, 25(1), 102-112 (1995).

11. Pera, J., R. Boumaza, and J. Ambroise, "Development of a Pozzolanic Pigment from Red Mud," *Cement and Concrete Res.*, 27 (10), 1513-1522 (1997).
12. Trauner, E. J., "Sludge Ash Bricks Fired to above and below Ash-Vitrifying Temperature," *ASCE J. Environ. Eng.*, 119(3), 506-519 (1993).
13. Anderson, M., R. G. Skerratt, J. P. Thomas, and S. D. Clay, "Case Study Involving Using Fluidized Bed Incinerator Sludge Ash as a Partial Clay Substitute in Brick Manufacture," *Water Sci. Technol.*, 34(3-4), 507-515 (1996).
14. Mindess, S., and J. F. Young, *Concrete*, Prentice-Hall, Inc., New Jersey (1981).

Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-chief within six months.

Manuscript Received: January 17, 2000
Revision Received: January 20, 2000
and Accepted: February 1, 2000

二次灼燒改良下水污泥灰渣卜作嵐活性及顆粒型態

曾 迪 華　潘 時 正

國立中央大學環境工程研究所

李 釗

國立中央大學土木工程學系

關鍵詞： 下水污泥灰渣，砂漿，卜作嵐反應，二次灼燒，飛灰

摘　要

下水污泥灰渣應用於砂漿以取代部份水泥，已由相關研究證明可行，但由於其顆粒型態不規則且具吸水性，同時卜作嵐活性不高，以致應用上受到限制。因此，本研究以高溫二次灼燒配合水淬處理，將污泥灰渣製備成二次灼燒灰渣，以改良其卜作嵐活性與顆粒型態。由試驗結果發現，污泥灰渣於1,000℃～1,200℃進行二次灼燒，並配合水淬處理，可將部份結晶性氧化矽轉變爲非結晶性氧化矽，導致卜作嵐強度活性指數明顯增加。其次由於灰渣在高溫下已近熔融狀態，因此污泥灰渣孔隙消失，灰渣磨細後表面變爲規則平滑。爲進一步確認二次灼燒改良灰渣卜作嵐活性及顆粒型態之效果，本研究選取1,200℃二次灼燒灰渣，與原污泥灰渣及飛灰進行取代砂漿水泥比較。結果發現在相同水泥取代量，使用二次灼燒灰渣不論在砂漿工作性及抗壓強度發展，均較使用原污泥灰渣有顯著改善，其性能更接近飛灰。依據以上發現，本研究認爲高溫二次灼燒配合水淬處理，爲一改良下水污泥灰渣卜作嵐活性及顆粒型態之有效方法。