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MICROSCOPIC STUDY OF ALKALI-ACTIVATED FLY ASH

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ABSTRACT

The activation mechanism of fly ash in a basic environment was studied as a means to improve the reactivity of fly ash in blended cements. The experimental program included activation of fly ash by a strong base (NaOH) at different concentrations, temperatures, and water-to-fly ash ratios.

It was found that the degree of reactivity, as shown by the compressive strength, increases with increasing concentration of the base (up to 4 mol of NaOH) and curing temperature (up to 90°C). Lowering the sodium hydroxide to fly ash ratio by lowering the water/fly ash ratio, while maintaining the solution concentration constant yielded a lower compressive strength in spite of the lower porosity, and the high concentration of the solution.

These results indicate that activation of fly ash in blended cements depends not only on the pH of the activating ambiance but also on the ratio between the latter and the fly ash. *© 1998 Elsevier Science Ltd*

Introduction

Several studies were published in the last decade on the activation of coal fly ash by an alkaline activator. Activation of volcanic ash by lime has been known since Roman times and has served as a means to produce ancient concrete (1). The use of fly ash together with Portland cement causes a reaction between the glassy phase of the fly ash and the calcium hydroxide generated during the hydration of the cement. This leads to the formation of additional C-S-H in the system, resulting in higher density and strength (2), thus allowing the replacement of part of the cement by fly ash.

Interest in the activation of fly ash has increased lately (3–7), motivated mainly by problems aroused by the disposal of nuclear waste, which is frequently of high alkalinity. Solidification of this waste in a cementitious material is one of the methods proposed for the disposal of this waste.

Recent studies on the solidification of Low Level Waste (LLW) have shown a high degree of reactivity of the fly ash particle, induced by the high alkalinity of the waste solution (8–10) when the process occurred at a relatively high water-to-binder (cementitious materials) ratio of 1.0 and at a high curing temperature of approximately 90°C. That temperature is, however, relatively low when compared with the work of Jiang et al. (11), in which a much higher temperature (200°C) was used for pre-treatment of the fly ash, and for the solidification of the

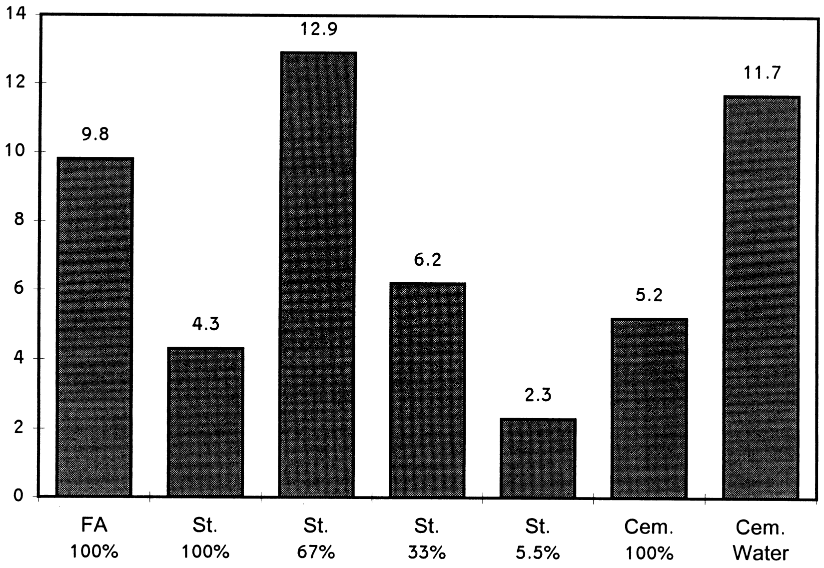

FIG. 1.
Compressive strength of fly ash (*FA*), fly ash:cement:attapulgite (68:21:11) (*St.*), and cement (*Cem.*) hydrated with alkali LLW solutions of different concentrations, cured at 90°C.

waste. Temperature development of up to 90–100°C, induced by an adiabatic temperature rise, had been observed by Lokken (12) when solidifying a large volume of LLW in vaults.

In the studies reported by LaRosa et al. (5) and Quillin et al. (4), lower temperature was used (up to 90°C). The purpose of these studies was to investigate the formation of different types of zeolites during the reaction between fly ash and an alkaline activator. In both studies, ordinary Portland cement (OPC) was used at a content of 20% in the first, and of 40% in the second study. The work of LaRosa et al. (5) was done at a low water-to-binder (w/b) ratio of 0.40, and a compressive strength of approximately 30 MPa was developed after curing for 14 days at 90°C. The activator was a 5 M NaOH solution, though the use of water glass ($Na_2O{\cdot}SiO_2$) is also common in works dealing with activation of blast furnace slag (13,14).

In the study of Katz et al. (10) on the solidification of high-alkalinity LLW in a mixture of fly ash, cement, and attapulgite clay (68%:21%:11%), a compressive strength of approximately 15 MPa was reached, when the w/b ratio was 1.0 at a curing temperature of 90°C. Zeolites were also found in this system (mainly gismondine and chabazite). Another work done by Katz and Brough (8) on fly ash alone, activated by the same solution in identical curing conditions, produced a relatively high compressive strength (9.9 MPa), as can be seen in Figure 1. Also presented in Figure 1 are the results for net cement mixed with water, the waste solution at the same w/b ratio (w/b = 1), and a mixture of fly ash, cement, and attapulgite (68%:21%:11%, respectively) mixed with the same waste solution at different concentrations. It appears that the high degree of activation of the fly ash by the alkali solution (see Fig. 2) led to improved compressive strength, which was higher than that of cement alone with the solution and almost as high as a system of net cement and water. Zeolite seemed to form in all of the fly ash systems.

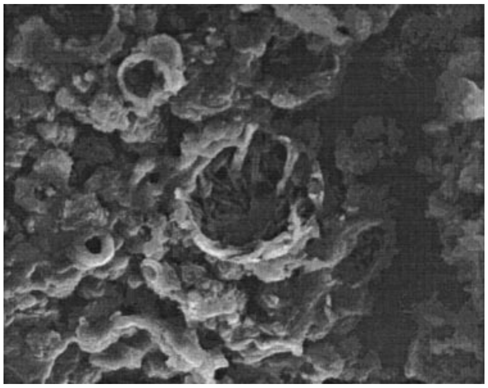

FIG. 2.
Micrograph of fly ash activated by LLW solution at 90°C.

In view of these results it was decided to further study the activation mechanism of fly ash by a highly alkaline solution, mainly the development of mechanical properties and microstructures under different conditions.

Experimental

Fly ash from a local power plant was tested. The mineral composition of the fly ash is presented in Table 1. A solution of sodium hydroxide was prepared immediately before mixing by using 250 grams of de-ionized water and the amount of NaOH needed for the desired concentration. Mixing was done with a small Hobart mixer at a low speed. The mix was cast into a 25 × 25 × 25 mm mold, which was sealed and placed in an oven at the testing temperature. After the mix had hardened sufficiently (usually after one day) it was demolded and placed again in the oven in a sealed container, in which a high humidity was maintained.

The testing program was divided into three parts: 1) studying the effect of NaOH concentration, 2) studying the effect of water/fly ash (w/FA) ratio, and 3) studying the effect of temperature.

Four sodium hydroxide concentrations were tested in the first part of the experimental program: 1 M, 2 M, 3 M, and 4 M. The water-to-fly ash ratio was 0.8 for all the mixes. The compressive strength was tested at 7 days after curing at 90°C. On considering the results it was decided to test the effects of the curing temperature and of the w/FA ratio on the 4 M solution only, and it was tested for curing at 90°C, 50°C, and 20°C, and with w/FA ratios of 0.4 and 0.8. In addition, a mixture of a high w/FA ratio of 10 was used to study the effect of excess NaOH on the activation process. For this purpose fly ash and 2 M and 4 M solutions

TABLE 1
Major minerals composition of the fly-ash (% by weight).

SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	P_2O_5
55.1	26.1	9.3	3.1	1.3	1.9	0.4

TABLE 2
Summary of the testing program.

Water/FA ratio	NaOH concentration	Water (gr.)	NaOH (gr.)	Fly-ash (gr.)	Curing temperature (°C)		
10.0	4 M	10	4	1		80	
	2 M	10	2	1		80	
0.8	4 M	250	40	312	90	50	20
	3 M	250	30	312		90	
	2 M	250	20	312		90	
	1 M	250	10	312		90	
0.4	4 M	250	40	625	90	50	20

were placed in a small container, which was kept rotating axially in an oven at a temperature of 80°C.

A summary of the testing program can be found in Table 2.

The fractured surface of all the specimens was observed under a Jeol 5300 Scanning Electron Microscope (SEM).

Results and Discussion

Effect of Solution Concentration

The effect of the concentration of the solution on the compressive strength at 7 days can be seen in Figure 3. It can be seen that for the same water-to-fly ash ratio and curing temperature the compressive strength increases with the concentration of the solution. At the low concentration of only 1 M, the hydration was very slow: the specimens could hardly be demolded after 4 days of curing at the high temperature and many of the cubes crumbled while demolding. After 7 days, the compressive strength was very low (0.2 MPa), due

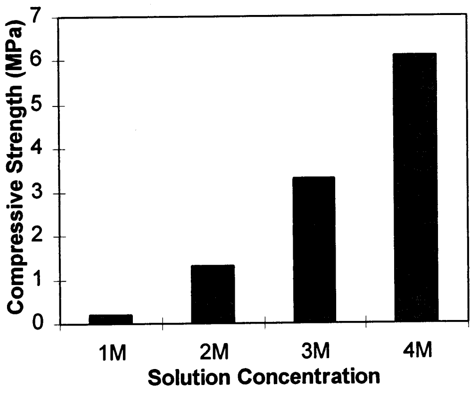

FIG. 3.
Effect of solution concentration on the compressive strength at 7 days.

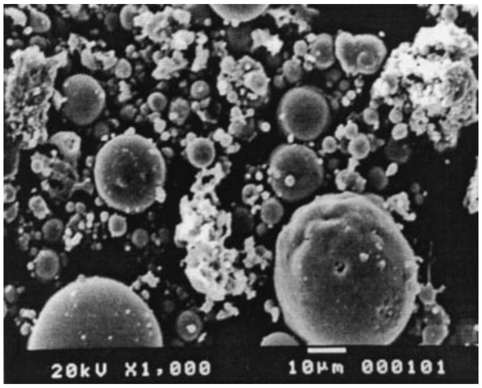

FIG. 4.
Micrograph of fly ash “as received.”

probably to weak Van-der-Vals forces between the small fly ash particles and not to the formation of hydration products.

The mixes of 4 M produced good mechanical properties, and a compressive strength of 6.1 MPa was obtained after 7 days, similar to the compressive strength of cement paste at the same age and water/cement ratio. Solution concentrations of 2 M and 3 M yielded compressive strength values in-between those produced by 1 M and 4 M solutions (see Fig. 3), which indicates that the degree of reactivity increases with the NaOH concentration.

Figures 4 through 8 show SEM micrographs of unreacted fly ash particles and fly ash reacted with the different solutions in ascending order of concentration. Figure 4 is a micrograph of the fly ash as received from the power plant. Most of the particles seen in this figure are round and smooth. Some of them are hemispheres containing small particles, as can be seen in the lower right-hand corner; others are clusters of particles, as can be seen in the upper right-hand corner of the figure.

The fly ash particles in Figure 5 (after 7 days of hydration in 1 M solution) seem quite similar to the ones in Figure 4. The surface of the particles seems to be as smooth as that of the unreacted fly ash, due to the low concentration of the solution (1 M) which was not strong

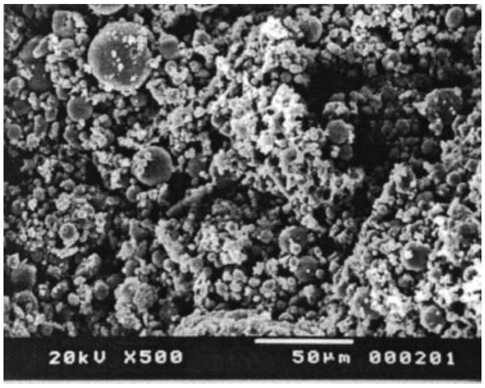

FIG. 5.
Micrograph of fly ash activated by 1 M of NaOH.

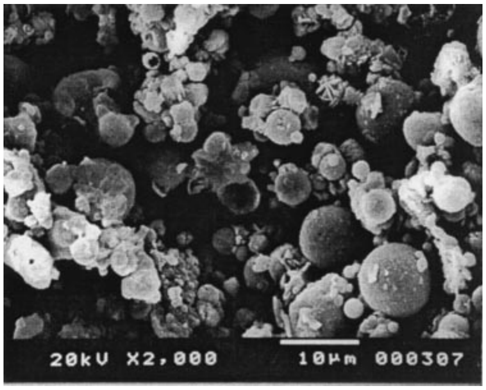

FIG. 6.
Micrograph of fly ash activated by 2 M of NaOH.

enough to react with the fly ash. More deeply etched particles can be seen in Figure 6 (2 M solution), and considerable etching in Figure 7 (3 M solution). In the latter, the glassy phase of the fly ash is seen to have dissolved extensively, exposing the mullite crystals known to be present in fly ash particles (15).

It seems that as the concentration of the solution increases, the degree of reactivity rises although the pH of the solution was relatively high from the very beginning of this series of tests.

Figure 8 shows a system of 4 M solution, presenting a substantially different microstructure. A more continuous matrix has formed, and the material appears to be more solid and less porous. The fly ash particles seem to be coated with a continuous matrix, which is rather different from the progressive etching of the fly ash particles observed in Figure 7 for the 3 M solution. It looks as if at this high concentration, the nature of the reaction between the sodium hydroxide and the fly ash has changed. In the 3 M system, needle-like crystals are seen between the fly ash particles (see Fig. 9). These needles are different from the needle-like mullite crystals seen in Figure 2 as the latter preserve the spherical shape of the original fly ash while the former are dispersed throughout the field. In the 4 M system, many

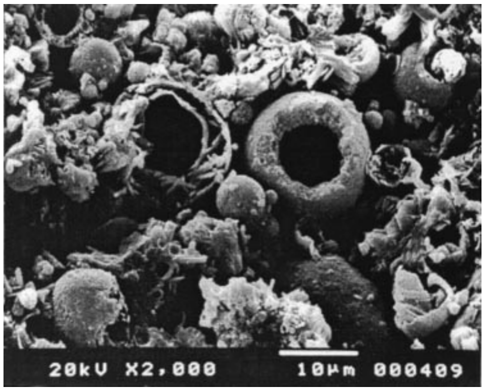

FIG. 7.
Micrograph of fly ash activated by 3 M of NaOH.

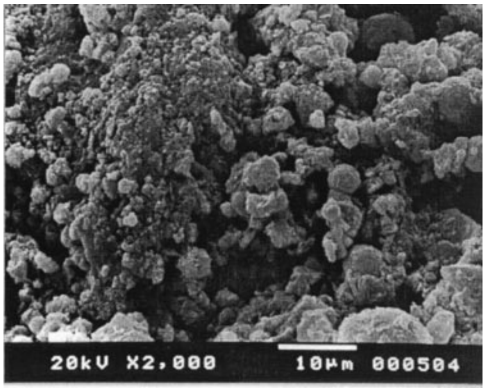

FIG. 8.
Micrograph of fly ash activated by 4 M of NaOH.

cubic crystals are observed (see Fig. 10), and no trace of the needle-like crystals is seen. Similar changes in the hydration products with increasing concentration of the activating solution were observed in the work of Katz et al. (10), in which Na-P1 (gismondine) was favored at one concentration and sodalite was favored at higher concentrations.

Effect of Curing Temperature and w/FA Ratio

In this series of experiments, the effects of curing temperature and the water/fly ash ratio were tested. The results are presented in Figure 11. It can be seen that the curing temperature has a considerable effect on the compressive strength of the material. At the low temperature of 20°C, almost no activity was observed, and the compressive strength produced by the high w/FA ratio was negligible. At the low w/FA ratio, some compressive strength could be measured (0.4 MPa), but this apparent strength is more likely a result of the denser packing of unreacted fly ash particles rather than a result of chemical activity of the system. The mix having a w/FA ratio of 0.8 did not set at this temperature, and no cubes could be prepared

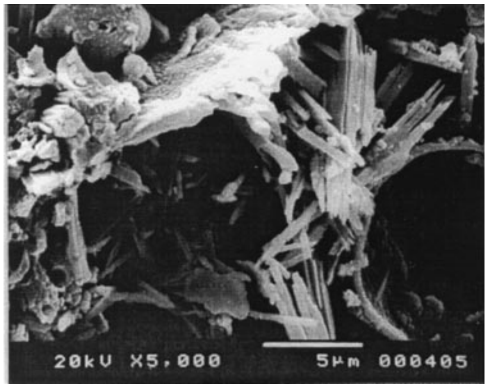

FIG. 9.
Needle-like crystals in the matrix between fly ash particles activated by 3 M solution.

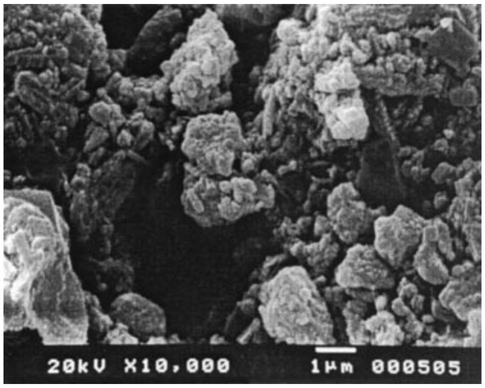

FIG. 10.
Cubic crystals in the matrix between fly ash particles activated by a 4 M solution.

for testing. It should be noted that a negligible compressive strength was observed in the work of LaRosa et al. (5) when alkali-activated fly ash was cured at room temperature for the same period of time.

At a higher curing temperature (50°C), a higher compressive strength was observed (0.9 and 1.75 MPa for the high and the low w/FA ratios, respectively), as can be seen in Figure 11. These results are relatively low, which indicate low reactivity at this temperature. At 90°C the compressive strength was much higher (6.2 and 4.9 MPa for the high and the low w/FA ratios, respectively), which indicates a higher reactivity of the material at this temperature.

It is interesting to note the combined effect of temperature and water/FA ratio on the compressive strength of the system. At low temperatures (20°C and 50°C), the hydration rate is probably low and the main contribution to the strength is made by the inter-particle forces. Thus, systems with denser initial packing exhibit higher compressive strength. At a higher

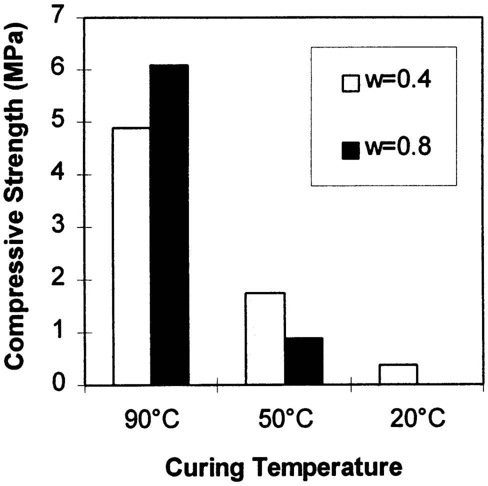

FIG. 11.
Effect of curing temperature and water/FA ratio on the compressive strength.

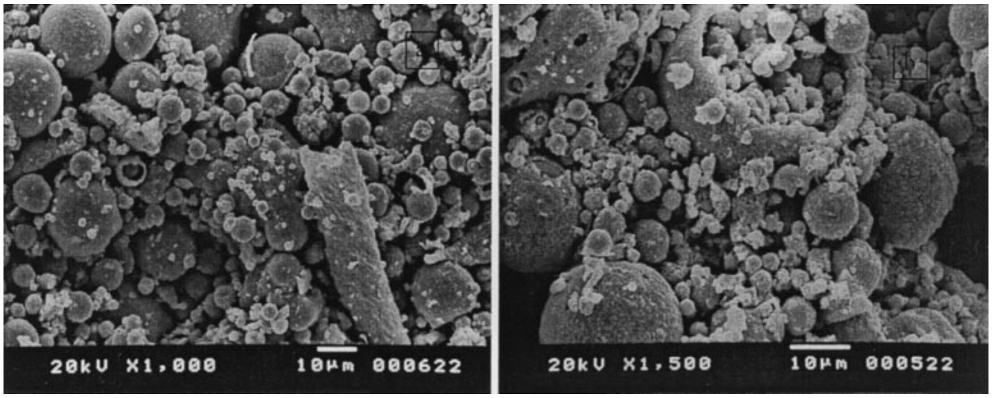

FIG. 12.
Mixes of low (*a*) and high (*b*) w/FA ratio, cured at 50°C, at low magnification.

curing temperature (90°C), however, different hydration products form (as can be seen in Figures 12 and 13), leading to a higher compressive strength of the system having the higher initial porosity. It is also possible that high pH of the solution is important for the initiation of the process, while the NaOH/FA ratio is also a significant parameter determining the type of hydration product forming in the process.

Differences between the effects of the low and the high w/FA ratios can also be seen in the SEM micrographs of the 4 M systems cured at 50°C, presented in Figures 12 and 13 at low and high magnifications, respectively. The system with the low w/FA ratio (Fig. 12a) is rich in slightly etched fly ash particles, whereas in the system with the high w/FA ratio (Fig. 12b), additional particles are seen that probably are products of the reaction between the fly ash and the sodium hydroxide. This reaction is combined with peeling of the reacted layer of the fly ash as can be seen at the higher magnifications in Figures 13a and 13b for w/FA = 0.4 and 0.8, respectively. In addition, differences are noted in the degree of reactivity in the two systems, observed by differences in the thickness of the reacted layer on the fly ash

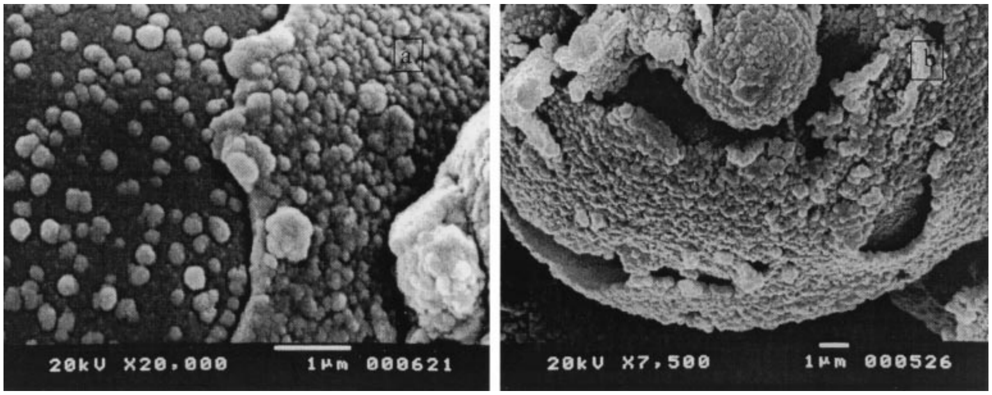

FIG. 13.
Mixes of low (*a*) and high (*b*) w/FA ratio, cured at 50°C, at high magnification.

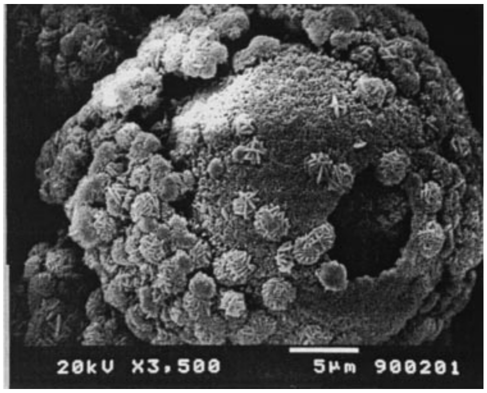

FIG. 14.
Fly ash of w/AF of 10, reacted with 2 M of NaOH and cured at 80°C.

particles in both Figures 12 and 13. Note the clear large reacted layer in Figure 13b despite the lower magnification compared with Figure 13a.

Samples prepared at a high w/FA ratio of 10 could not gain any compressive strength, and they were tested under the SEM only. Figures 14 and 15 compare the two systems, the former prepared with 2 M solution and the latter with 4 M solution. It is seen from the figures that the reaction products are intrinsically different. All fly ash particles, hydrated in the 2 M solution were covered with small spheres (approximately a diameter of 2 μm) of needle-like materials that had been dissolved from the fly ash and had recrystallized on its surface. Spheres of the same type were seen in the work of LaRosa et al. (6), and are believed to be zeolite crystals.

The surface of the fly ash particle hydrated in the 4 M solution (Fig. 15) looks quite different. It is not clear whether the figure represents the etched surface of a fly ash particle from which the solid material has moved into the solution or a new type of crystals which formed on the surface of the particles. The second assumption seems the more reasonable, as complete dissolution of the glassy phase would leave the mullite skeleton exposed, as was seen in Figures 2 and 7. Thus it is possible that a different type of crystal has indeed formed,

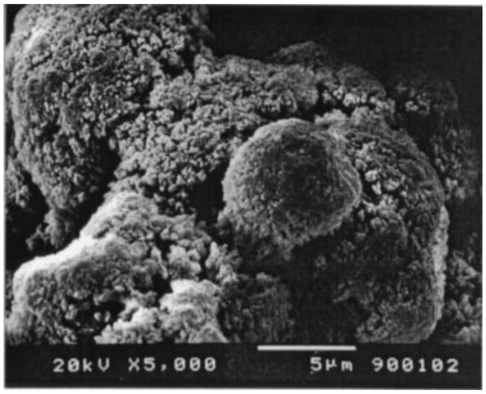

FIG. 15.
Fly ash of w/AF of 10, reacted with 4 M of NaOH and cured at 80°C.

as also happened when the concentration of the solution was increased from 3 M to 4 M, as discussed earlier. SEM observations at higher magnifications of the particle surface could support this assumption, but it was difficult to obtain good quality micrographs of sufficiently high magnification. Additional X-Ray Diffraction (XRD) is needed in order to strengthen this assumption.

Conclusion

1. Fly ash was reacted with sodium hydroxide solutions of different concentrations, and it appeared that the higher the concentration of the solution, the higher is the reactivity of the material. SEM observations showed higher reactivity as the concentration of the solution is increased. At a concentration of 4 M, a continuous solid material was observed, while etching of the fly ash particles to different extents could be seen at the lower concentrations.
2. It seems that no reaction took place at room temperature, and higher temperatures are needed for activating the fly ash. A relatively high compressive strength was observed at 90°C despite the high water/fly ash ratio, indicating a relatively high degree of reactivity.
3. Lowering the water/fly ash ratio did not result in a higher compressive strength, but rather a lower one. SEM observation showed a higher degree of reaction on the fly ash particles of the higher water/FA ratio. It is possible that the ratio between the activating material and the fly ash is of importance in addition to the degree of alkalinity of the solution.
4. SEM observations showed different microstructures of the system affected by curing temperature, solution concentration, and w/FA ratio. The differences were mainly in the manner of the etching and in the type of crystals formed.
5. Additional studies are needed in order to better understand the activation mechanism of fly ash by the alkali environment, its stability at lower temperatures, and the potential use of this material as a means to stabilize hazardous materials.

Acknowledgment

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