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Dissolution properties of some fly ash fillers applying to geopolymeric materials in alkali solution

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Abstract: Dissolution properties of three kinds of fly ash including a Pressurized Fluidized Bed Combustion (PFBC)ash from a novel type of fluidized bed combustion boiler have been studied by leaching in different concentrations of caustic soda solution up to 15 N at 25 °C and 80 °C, stirring for 1 h with liquor/solid ratio = 10. Liquors sampled by a centrifugal separator were chemically analyzed by ICP technique. A blast furnace slag was also studied for reference. Results showed that Ca^{2+} dissolved relatively large amount in genuine water, but no marked dissolution was detected with increasing NaOH concentrations of the leaching solution. No enhanced dissolution of Al^{3+} was detected for ordinary fly ashes collected from pulverized coal combustion boilers even with increasing concentrations of solution at 25 °C, whereas enhanced dissolution of Al^{3+} was observed at 80 °C, when 5 N was reached and more. On the contrary, appreciable increasing was noted on the dissolution of Si^{4+} with increasing NaOH concentrations even at 25 °C for the ordinary fly ashes and the Si^{4+} dissolution became enhanced at 80 °C, specifically in 5 N and more.

Introduction

The 21st century is called ‘‘the age of environment’’ and so many urgent problems remain to be solved. Above all, carbon dioxide reduction policy so called Kyoto protocol or COP3 issued in 1997 and sea conservation policy to prohibit waste dumping to open seas so called London protocol issued in 1996 are urgent big two. Among these circumstances, the geopolymer technique is currently expected as a novel technique to solve these problems simultaneously. The geopolymer process emits less carbon dioxide and it is said that 80% reduction is possible against the Portland cement process [1]. Furthermore, most of mineral powders can be solidified by the geopolymer technique into monoliths only by blending so called ‘‘active fillers’’ [2].

The generation rate of geopolymers is closely related to the dissolution properties of metallic ions dissolving from fillers in alkali solution. In this context, it is very important to study metallic ion concentrations leached out of fillers in solution.

There has been a lot of works studied on dissolution tests of geopolymer materials [3–12] for immobilizing toxic metals, reduction of metal leaching etc. However, there are few references on dissolution tests of waste origin in alkali condition. Recently, extensive studies of dissolution were carried out for calcined kaolins and pyrophyllites in alkali conditions [13, 14]. In this paper, dissolution properties of mineral fillers of waste origin will be investigated.

Experimental

Three kinds of fly ash of coal origin discharged from pulverized coal combustion boiler plants designated as

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OF-C and OF-U, and a novel type fly ash so called PFBC ash or PF-ash in short discharged from a pressurized fluidized bed combustion boiler here designated as PF-C were studied. It should be stressed that this type of ash is discharged from novel type of powder plants called ''pressurized fluidized bed combustion boilers'' different from current ''pulverized coal combustion boilers'' widely accepted all over the world. PF-ash is characterized by a peculiar chemical compositions, i.e., high CaO and SO_3 contents originated from limestones premixed with coal to prevent air pollution caused by flue gas. In addition, water quenched granulated blast furnace slag supplied from a steel plant designated as SL-S was studied as reference. Chemical compositions of these fillers were analyzed by XRF spectrometer, Rigaku ZSX-101e, employing the conventional borax bead technique.

Dissolution tests of these four kinds of powder were conducted in alkali conditions at 25 °C and 80 °C with constant stirring for 1 h duration. Primarily, 5 g sample was taken in a 100 ml plastic beaker covered with a lid and then caustic soda solution of different concentrations, generally up to 15 N, was pored as much as 50 ml. Therefore, liquor/solid ratio was 10. Warming the solution was performed by a laboratory magnetic stirrer equipped with a water bath. Liquor portion was collected by a centrifugal separator. Thus, concentrations of metallic ions leached out of the filler samples into the liquor were determined on Ca^{2+}, Al^{3+} and Si^{4+} species by ICP technique, employing a Varian VIST analyzer. XRD apparatus, Rigaku RINT-2500HF diffractometer was conveniently used to examine the fillers as well as some run products.

Results and discussion

Sample characterization

Chemical compositions of present fillers are shown in Table 1. PF-C was characterized by high CaO- and SO_3–components due to high sulfur coal combustions. LOI, loss on ignition, exceeded 5 percent, mostly due to the remaining free carbon. OF-C had a chemical composition typical to ordinary fly ash and LOI was less than 5 percent due to the efficient combustion of most modern type boiler. OF-U had also such a typical chemical composition, but LOI exceeded 5 percent due to old type boiler. The 5 percent LOI is believed to be a criterion of colors of ash, dark gray or light gray. When LOI is more than 5 percent, the ash exhibits dark gray in color. On the other hand, chemical composition of SL-S is represented by high CaO- and MgO-components as well as somewhat high SO_3–component.

XRD charts of present fillers are shown in Fig. 1. According to XRD, quartz was observed as intrinsic

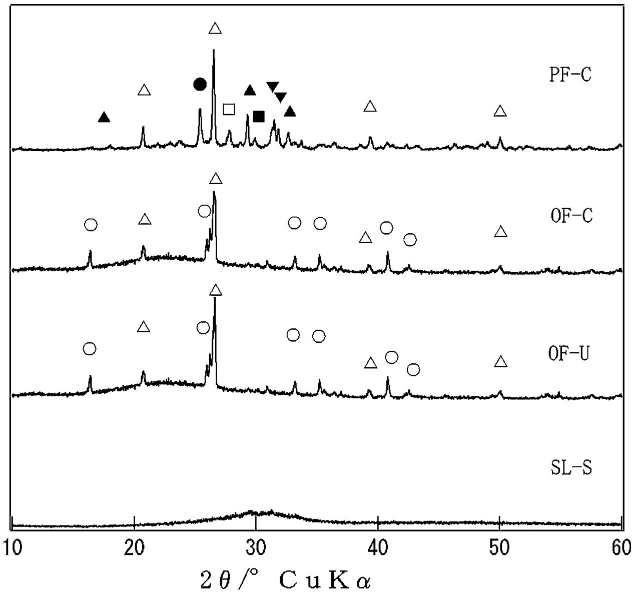

Fig. 1 XRD patterns of raw materials of waste origin. ▲- $Ca(OH)_2$, △- SiO_2, ■- $CaCO_3$, ●- $CaSO_4$, ○- $Al_6Si_2O_{13}$, □- $CaAl_2Si_2O_8$, ▼- $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$

Table 1 Chemical compositions of fillers and relevant physical properties

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	SO_3	P_2O_5	LOI	Total
PF-C	39.12	0.64	16.74	2.96	0.02	24.95	0.80	0.60	0.46	8.75	0.22	5.57	100.83
OF-C	60.02	1.18	23.71	5.19	0.04	2.68	0.93	0.48	0.48	0.18	0.48	3.62	99.55
OF-U	68.19	0.99	16.75	2.48	0.03	0.83	0.47	0.82	0.82	0.50	0.15	7.77	100.06
SL-S	31.37	0.63	14.70	0.30	0.32	44.04	5.99	0.45	0.45	0.04	0.04	–	99.99
	Specific gravity	Specific surface area, Blaine, cm^2/ g	Specific surface area, BET, m^2/g										
PF-C	2.39	5680	3.65										
OF-C	2.39	4546	3.39										
OF-U	2.20	2483	3.48										
SL-S	2.45	1382	1.38										

mineral for PF-C. Formation of anhydrite, anorthite and hydroxyl ellestadite, $Ca_{10}(SiO_4)_3(SO_4)_3(OH)_2$ was identified as reaction products during combustion. Moreover, free CaO was detected in minor as portlandite and calcite. It is well-known that pressurized fluidized bed combustion boiler ash, PFBC-ash or PF-ash in short, has no glassy phase due to low temperature combustion around 860 °C and exhibits fragmental grains in shape. Some mullite and quartz are identified other than glassy phase for ordinary fly ash, OF-C and OF-U due to high temperature combustion around 1500 °C. This type of ash exhibits glassy globules in shape. The slag, SL-S was completely amorphous and glassy due to water quenching.

The 3-point BET analysis showed high specific surface area for the three kinds of fly ash, whereas low specific surface area for the slag due to high grade glassy powder.

Dissolution of CaO-component

Results of the dissolution test are summarized in Figs. 2 and 3 as a function of NaOH concentration up to 1 N. In genuine water, considerably high dissolution was observed in all the fillers except SL-S, specifically in PF-C due to containing free CaO. With increasing NaOH concentration, however, the dissolution was suddenly decreased and portlandite precipitation was noted by XRD with no appreciable carbonation. Therefore, it can be said that decreasing Ca^{2+} ions so sharp with increasing NaOH concentrations are due to the precipitation of portlandite. There was not so much difference between 25 °C and 80 °C leaching. However, it is very strange that somewhat high dissolution was noted in some samples such as PF-C and SL-S in high NaOH concentration ranges, specifically in 80 °C leaching. These two samples are characterized by containing high CaO-component as well as SO_3–component. Therefore, it is considered that the SO_3–component may suppress increasing pH of solution, resulting the somewhat high dissolution of Ca^{2+} species in high NaOH concentration ranges.

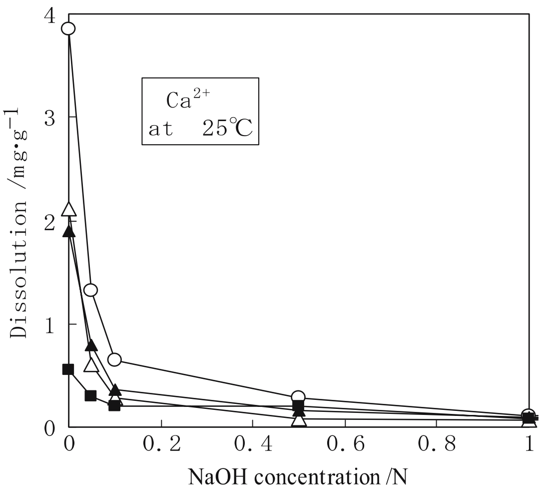

Fig. 2 Dissolution of Ca^{2+} as a function of NaOH concentration of leaching solution at 25 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

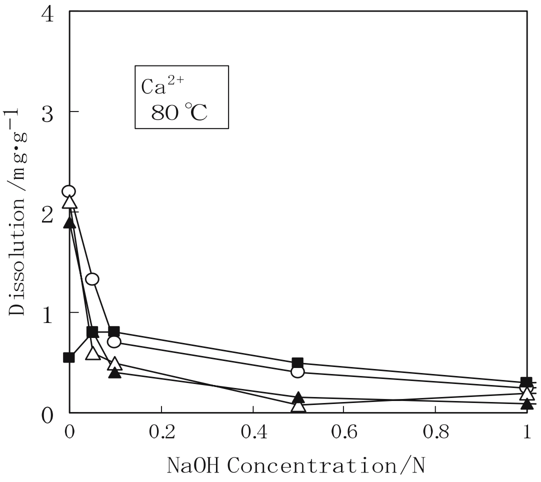

Fig. 3 Dissolution of Ca^{2+} as a function of NaOH concentration of leaching solution at 80 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

Blast furnace slags are generally inactive in genuine water and become active in alkali conditions caused by the effects so called stimulation and activation. However, little Ca^{2+} dissolution was noted even in alkali regions probably due to topotactic hydration nature of the slag. Furthermore, this decreasing may also closely related to relatively small dissolution of Si^{4+} ions in the Ca-rich fillers as mentioned later (Figs. 6 and 7), precipitating C-S-H gel.

Dissolution of Al_2O_3–component

Dissolution properties of Al_2O_3–component are shown in Figs. 4 and 5 in terms of Al^{3+} versus NaOH concentrations up to 15 N. No appreciable dissolution was noted in genuine water conditions for both 25 °C and 80 °C leachings. However, some dissolution was detected with increasing NaOH concentration. Al^{3+} began to dissolve around 5 N and more in 25 °C leaching, whereas around 1 N and more in 80 °C leaching.

In 25 °C leaching, dissolution of the slag, SL-S was so markedly increased with NaOH concentration. The Ca-rich coal ash, PF-C exhibited a saturated dissolution at 10 N and more probably due to some precipitation of Ca-aluminate hydrates. The ordinary coal ashes, OF-C and OF-U showed not so marked dissolution even in very high NaOH concentrations.

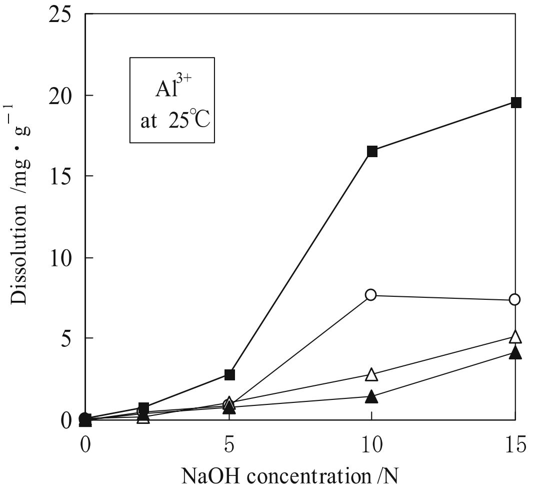

Fig. 4 Dissolution of A1^{3+} as a function of NaOH concentration of leaching solution at 25 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

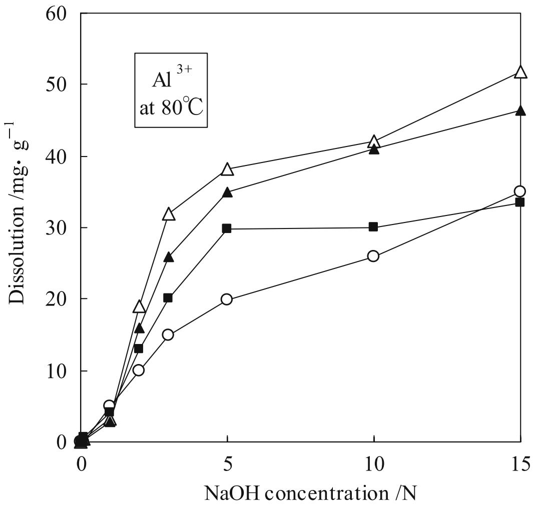

Fig. 5 Dissolution of A1^{3+} as a function of NaOH concentration of leaching solution at 80 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

On the contrary, in 80 °C leaching, all the fillers showed relatively high dissolution with increasing NaOH concentration. Specifically, dissolution of the ordinary fly ashes increased remarkably to the level of 40–50 mg · g^{-1}. Dissolution of the Ca-rich coal, PF-C was also increased. However, saturation was noted on the slag, SL-S also rich in CaO-component probably due to the formation of Ca-aluminate hydrates as well as ettringite and Ca-monosulphate hydrate.

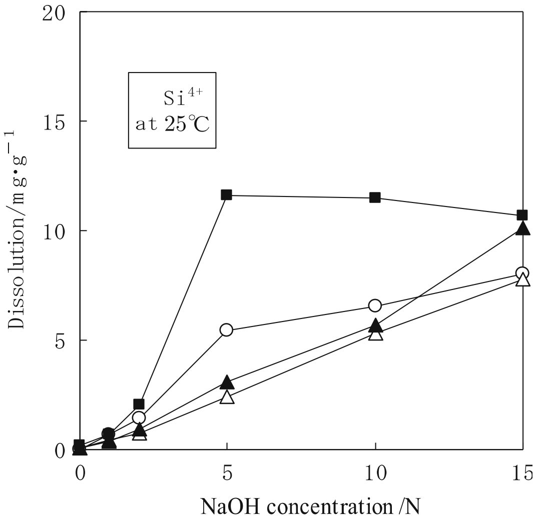

Fig. 6 Dissolution of Si^{4+} as a function of NaOH concentration of leaching solution at 25 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

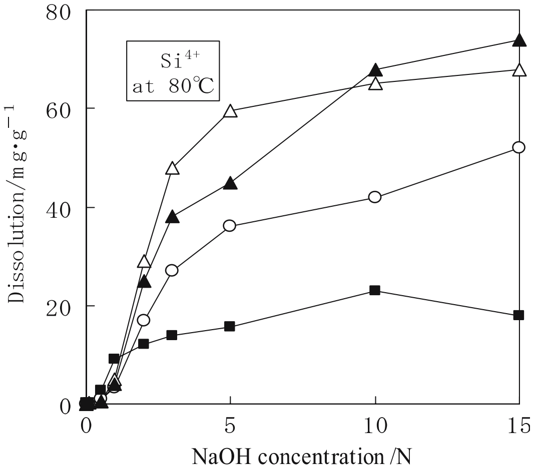

Fig. 7 Dissolution of Si^{4+} as a function of NaOH concentration of leaching solution at 80 °C. ○- PF-C, △- OF-C, ▲- OF-U, ■- SL-S

Dissolution of SiO_2–component

Dissolution properties of SiO_2–component are shown in Figs. 6 and 7 in terms of Si^{4+} versus NaOH concentrations up to 15 N. No appreciable dissolution was noted in genuine water conditions for both 25 °C and 80 °C leachings. However, some dissolution was detected with increasing NaOH concentration. Si^{4+} began to dissolve around 2 N and more in 25 °C and 80 °C leachings, which are different from the results of Al^{3+} dissolution.

In 25 °C leaching, saturated and decreased dissolution was noted on the slag, SL-S at 5 N and more probably due to the precipitation of C-S-H gel. The CaO-rich coal ash, PF-C showed moderately increasing dissolution. The ordinary coal ashes, OF-C and OF-U showed also increasing dissolution.

In 80 °C leaching, remarkably high dissolution was noted on the coal ashes, specifically on the ordinary fly ashes, OF-C and OF-U and 40–70 mg · g^{-1} dissolution was ultimately reached in very high NaOH concentration regions. However, saturation was detected on the slag, SL-S probably due to the topotactic formation of C-S-H gel, which suppresses dissolution out of the fillers to the external liquor. The CaO-rich filler, PF-C showed moderately high dissolution without saturation.

Conclusion

Measurements of dissolution of fillers have been carried out in caustic soda solutions up to 15 N concentration at 25 °C and 80 °C, using three kinds of fly ash and one kind of water quenched granulated blast furnace slag in order to grasp some basic dissolution knowledges for fillers applied to geopolymeric monoliths. The obtained dissolution properties can be summarized as follows.

Appreciable amount of dissolution is noted on CaO-component in genuine water for the coal ashes specifically for PF-ash rich in CaO, whereas that is not marked for the slag despite rich in CaO. Increasing NaOH concentrations of leaching solution suppress the Ca^{2+} dissolution to precipitate portlandite irrespective of leaching temperature.

Dissolution of Al_2O_3–component is not so marked in 25 °C leaching irrespective of NaOH concentrations of leaching solution for ordinary coal ashes discharged from pulverized coal power plants. However, high dissolution has been found in 80 °C leaching even for the ordinary coal ashes of which dissolution becomes enhanced, when exceeding around 5 N concentration. High dissolution is noted for the slag even in 25 °C leaching, when exceeding around 10 N concentration. PF-ash shows moderately high dissolution even in 25 °C leaching according to increasing NaOH concentrations, but saturation was encountered at high NaOH concentration regions exceeding 10 N presumably due to precipitation of Ca-aluminate hydrates.

Increasing dissolution of SiO_2–component in relatively high amount is noted in 25 °C leaching with increasing NaOH concentrations even for the ordinary coal ashes discharged from pulverized coal power plants as well as for PF-ash. The dissolution becomes enhanced in 80 °C leaching, when exceeding around 5 N concentration. Saturated dissolution has been encountered for the slag irrespective of leaching temperature, presumably due to the formation of C-S-H gel.

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