Preparation of geopolymeric materials from sewage sludge slag with special emphasis to the matrix compositions

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Solidification of SSS (sewage sludge slag) has been carried out by the geopolymer binder technique at 80°C steam conditions mixed with CFA (coal fly ash). Geopolymer liquor was prepared by mixing Na-disilicate solution of 1.27 S.G. (specific gravity) and 10 M NaOH solution in 3:1 proportion. Obtained monolithic materials were subjected to physical measurements such as 3-point flexural strength, bulk density and expansion-shrinkage. Subsequently, matrix as well as filler chemical compositions were analyzed by SEM–EDX. Results showed SSS is an active filler similar to CFA and maximal strength was reached by blending SSS with CFA in 1:3 proportion. P_2O_5 and CaO components of SSS strongly contributed to the polycondensation of the geopolymer liquor other than theoretically expected Al_2O_3 and SiO_2 components.

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1. Introduction

Recently, the geopolymer binder technique is attracting special attention as presenting novel inorganic binders other than traditionally accepted cementitious binders mostly represented by Portland cements. The geopolymer binder technique is not dependent on limestone so that this technique is able to contribute greatly to the current environmental issues such as "green house effect" and "waste recycling". It is said that 80% reduction of carbon dioxide emissions is attained, when compared with Portland cement manufactures.¹⁾ Furthermore, solidification of wastes tremendously discharged from coal boilers as well as other waste treatment plants is possible by making monolithic materials.^{2),3)} Geopolymer binders belong to inorganic polymers based on polycondensation of [Si(OH)₄]-complexes,⁴⁾ typically seen in silica gel formation in acidic conditions, which yields well-known siloxane structures, -O-Si-O-Si-O-. However, this polycondensation never takes place in basic conditions and some incorporation of foreign metallic ions is required to yield polycondensation, resulting bridging structures, -O-Si-O-M-O-Si-O-, where M denotes foreign metallic ions with polyvalence. Although there are several sources for [Si(OH)₄]-complex including TEOS, alkali-silicates are conveniently used from the economic point of view. Among others, sodium-silicates, wellknown as water glasses, are commercially available in large amounts. It should be bear in mind that if the foreign metallic ions are added in a form of solution to the alkali-silicate solutions, this bridging polycondensation so suddenly takes place, resulting so-called "flash setting". To avoid this, mineral powders called fillers having moderate dissolutions to alkali solutions are introduced. Such powders are called "active fillers" and several ones have been found so far.⁵⁾⁻⁸⁾ Among others, metakaolins are typical active fillers and have superior properties, but expensive. To the contrary, coal fly ashes are inexpensive and can be used as alternatives of metakaolins. When mixed with an alkali-silicate solution, some amount of metallic ions dissolve slowly from the active fillers into the surrounding alkali-silicate solution so that gradual polycondensation and solidification take place to obtain eventually monolithic materials as illustrated in Fig. 1. Thereby, it is considered that dissolutions of Al³⁺ ions as well as Si⁴⁺ ions play a major role.¹⁾⁻³⁾ These dissolutions can be regarded as a kind of leaching and sometimes called "elutions" in other words. Although this type of solidification proceeds even at room temperature, worming conditions are generally recommended to accelerate the polycondensation process. Fillers having inadequate dissolutions are called "inactive fillers", which have scarce capability of solidification. However, monolithic materials can be obtained by mixing some amount of active fillers together.⁹⁾ In addition, coal fly ashes are well-known as active fillers as mentioned, but filler characteristics of sewage sludge slags have not so well been studied so far.

Geopolymer binders are superior to Portland cement binders as represented by following five respects. The first is very low amount of carbon dioxide emission as mentioned. The second is solidification capabilities of wide range of wastes, even contain-

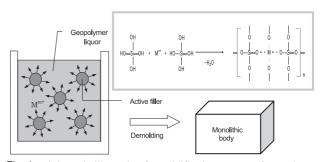


Fig. 1. Schematic illustration for solidification process of geopolymer binders.

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ing hazardous heavy metals. For instance, lead, which is not sufficiently immobilized by Portland cement binders, is immobilized by geopolymer binders below bench mark.¹⁰⁾ Furthermore, even nuclear wastes can be solidified in safe.¹¹⁾ The third is highly resistant to sulfuric acid as well as to sulfuric salts. This property is lacking to Portland cements and massive applications to sewer pipes as well as marine and geothermal constructions are expected.¹²⁾ The fourth is high thermal resistance up to 1000°C. Incidentally, that is up to 400°C for Portland cements, since hardened geopolymer binders are composed of amorphous materials so-called "zeolitic gels" showing no discrete dehydration points. To the contrary, Portland cement binders consisting of crystalline and semi-crystalline materials so-called "hydrates" show discrete dehydration points, which eventually spoil hardened Portland cement bodies so serious. The fifth is excellent durability. Extremely long material life is expected, say over 1000 years, since geopolymer bodies are free from carbonation occurring in atmosphere, which leads to cracks and rust of hardened Portland cement bodies, specifically in case of steel reinforcement.

In modern cities in Japan as well as in the world, human excreta is drained through sewer pipes together with waste water from kitchens and lavatories and is finally treated at sewage disposal plants. Therefore, no need to say, installations of flush toilets are required. Introduction of disposers to kitchens is not recommended in Japan, almost prohibited, in order to prevent the disposal plants from overburdens. In addition, some rain fall water has been drained in Japan through sewer pipes, but this old system is gradually being improved by separating the drainage pipes into rain fall own.

In sewage disposal plants, treatment and precipitation of solid wastes from the collected muddy water are conducted through biochemical process called "the activated sludge technique" to obtain finally sewage sludge. The output water of counter part is further cleaned and discharged to rivers, lakes and seas after regulating pH values, while the remaining sludge after treatment is stocked in the plant yards to dump to land-fill. Sometimes composts are made from the sludge, since the sludge is rich in phosphorous components and still contain some organics.

It should be referred to that in heavily inhabited cities to maintain large stock yards as well as land-fill sites is becoming very difficult year by year. In such cities volume reduction of the sludge is frequently performed by melting the sludge in furnaces which work with methane evolved during the treatment process. The resulting glassy wastes are called "swage sludge slag" or simply "slag". This fusion process is similar to the volume reduction for urban refuse incineration ash. The volume is reduced to one thirties by fusion. However, major difference between the urban incineration ash and the sewage sludge is the concentration of pollutants, mostly heavy metals such as lead and so on. The former is highly contaminated with heavy metals in addition to dioxin, while the latter is less contaminated. Therefore, in this respect, recycling of sewage wastes, including both of sludge and slag, are safe to environment, if there are any hopeful measures for recycling. In this respect, making bricks were tentatively performed by sintering the slag in some municipal governments. Production of sand alternatives for concretes was also another attempt.

Annual output of overall wastes is 406 million tons in Japan.¹³⁾ The share of sludge and slime is 46.6% corresponding to 189 million tons. Although a part of them has been recycled, the rest has been discarded to open seas for a long time including sewage sludge. However, this conventional discarding is now prohibited

by the London protocol issued 1995, declaring prevention of sea waters from contaminations including muddy wastes. Since then, land discarding is now the only way, which leads to increasing slag plants in number on lands.

Standing on this background mentioned above, novel recycling technique of sewage sludge slag will be studied in this paper by consolidating the slag with geopolymer binders.

2. Experimental

According to literature,¹⁴⁾ the geopolymer liquor was prepared from JIS No.1 water glass commercially available and caustic soda pellets, Sigma-Aldrich Ltd., JIS 1st grade. The as-received water glass was in solution, which was diluted with deionized water to obtain 1.27 S.G., specific gravity, solution, corresponding to 1.69 M Na₂O·2SiO₂ concentration. Similarly, the caustic soda pellets were dissolved to obtain 10 M NaOH solution. Then, these two solutions were mixed together in 3:1 proportion by volume and kept standing at least 3 h before use. This 3:1 mix is very important to maintain shape stabilities of the hardened bodies. If other proportions other than around 3:1 are used, stable hardened bodies never obtained in dimensions, showing expansion and shrinkage which eventually lead to bendings and crackings of the bodies. The extra strong alkali solutions are called "activate solutions" or simply "activators" and generally more than 8 M is required in concentration in case of NaOH. In addition, the mixed solutions consisting of alkali silicates and strong alkalis are often called "geopolymer liquors" altogether.

Monolithic materials were prepared from the mixtures of sewage sludge slag, hereafter called SSS, and coal fly ash, hereafter called CFA, in 25% intervals. The amount of CFA is labeled, for instance, as R75 meaning 75% dosage of CFA. The SSS was supplied from a municipal plant located at northern part of Nagasaki prefecture, while the CFA, pulverized bituminous coal boiler origin, was supplied from a power plant located at Southwestern part of Yamaguchi prefecture. The as-received SSS was in beads around 5 mm in size, exhibiting brown to black in color and completely odorless, which was pulverized into fine powder employing a laboratory ball mill with water media and finally dried in an oven. This lot is called SW2 of laboratory label. The CFA was applied as-received. This lot is called OF12 of laboratory label. The chemical compositions of these fillers are determined by X-ray fluorescent spectrometry, XRF, employing Phillips, MagixPro with borax bead technique. Relevant physicochemical characteristics of present raw materials are tabulated in Table 1.

Each butch weighed as much as 160 g was well-mixed in a bottle and transferred to a 500 mL plastic beaker. Then, the geopolymer liquor was flooded in proportions of 0.43 W/S, where W and S are corresponding to the geopolymer liquor and the fillers by weight, respectively, and then, hand-mixed with a laboratory spoon for 1 min. Subsequently, the charge was cast into a

Table 1. Physico-chemical Characteristics of Raw Materials

Specific surface area and apparent density									
Swage sludge slag (SSS, Laboratory label SW2)	3820 cm ² /g, Blaine 2.67 g/cm ³								
Coal fly ash (CFA, Laboratory label OF12)	4640 cm ² /g, Blaine 2.22 g/cm ³								
Geopolymer liquor (Silica source:Activ	vator = 3:1 by volume)								
Silica source: Commercial JIS No. 1 water glass d (1.69 M as Na ₂ O-2SiO ₂)	iluted to 1.27 S.G.								
Activation: Caustic soda IIS 1st grade reagent disso	lved to 1 31 S G (10 M as NaOH)								

Activatior: Caustic soda, JIS 1st grade reagent dissolved to 1.31 S.G. (10 M as NaOH)

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Main component															
Filler*	Label*	SiO_2	TiO ₂	Al_2O_3	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K_2O	SO_3	P_2O_5	LOI	$\sum 1$	
SSS	WS2	22.20	0.81	18.41	5.27	0.10	12.81	5.57	2.33	1.86	-	27.50	_	96.86	
CFA	OF12	62.70	1.01	21.59	5.40	0.07	2.15	0.96	0.32	1.47	0.58	0.15	2.88	99.28	
					-	Minor co	mponent	over 0.1%	, 0						
Filler*	Label*	ZrO_2	Cr_2O_3	SrO	BaO	CuO	ZnO	$\Sigma 2$	Grand total $(\Sigma 1 + \Sigma 2)$						
SSS	WS2	0.13	0.25	0.28	1.50	0.26	0.37	2.79	99.65						
CFA	OF12	0.19	_	0.12	0.11	_	_	0.42	99.70						
-															

Table 2. XRF Results of Chemical Compositions for Raw Fillers

*Refer to Table 1 -: trace

mold consisting of three prismatic cells, each having $20 \times 20 \times$ 80 mm dimension. After standing for 1 h at room temperature, the charged molds were put into a steam oven, Tabai, LHL-112 and cured at 80°C and 80%RH conditions for 24 h. The demolded specimens were kept at room temperature for 1 d followed by some physical tests, which were bulk densities, expansion and shrinkage as well as 3-point flexural strength. Bulk densities were determined from the weight and dimension of specimens. Similarly, expansion and shrinkage were determined on the basis of the long edge length of molds and specimens by measuring with a digital caliper. The beam fracture test was conducted by a strength tester, Orientec, Tensiron RTC-1250 A at constant cross-head speed of 0.2 mm/min with 50 mm span. Then, the 3-point flexural strength was determined, applying the formula, $\sigma_f = \{(3/2)L/wh^2\}$ P, where σ_f , L, w, h and P denote flexural strength, span, width, height and fracture load of specimens, respectively. Finally, all the data were averaged on 3 test-pieces for 1 test point to obtain final data according to convention.

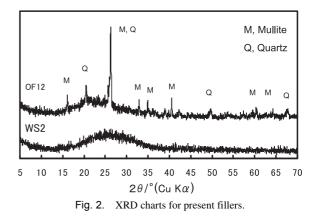
An X-ray diffractometry apparatus, XRD, Phillips, MPD1880, 40 kV-30 mA, and a scanning electron microscopy apparatus equipped with energy dispersive X-ray spectrometry function, SEM–EDX, JEOL Ltd., JSM–6300F, 20 kV, and Thermo Fisher Scientific, Noran System 7 were employed, respectively, in order to identify crystalline phases and to observe solidified features of obtained hardened bodies in addition to analyze chemical species consisting of matrices and fillers with carbon coating. Obtained X-ray data were finalized by the ZAF technique normalizing to 100.

Results and discussion

3.1 XRF and XRD of raw fillers

As seen in **Table 2**, the SSS is characterized by the phosphorous component, which is enormously high, reflecting the human excreta origin. In addition, the calcium component is also high, which is originated from the lime added to in the course of treatment process of the disposal plant as precipitating and deodorant agents. Magnesium content is also rather high. It should be mentioned that minor components share 2.79% of overall and this is considerably high. Specifically, Cr_2O_3 component is very much hazardous, if reaching out in hexa-valent state, but long term monitoring in the disposal plant shows under bench mark at the moment.

The chemical composition of the CFA is usual one, showing chemical compositions typical to bituminous coal origin. Consequently, the present CFA belongs to so-called the low-lime type.



The specific surface area was higher, showing over $4000 \text{ cm}^2/\text{g}$, Blaine. According to authors' experience, more than $4000 \text{ cm}^2/\text{g}$ is required for stable solidification of CFA fillers. When LOI, loss on ignition, value exceeds 5%, CFA begins to exhibit black in color. The present CFA, showing less than 3% LOI, indicates light gray in color. Incidentally, LOI values are mostly corresponding to the amounts of free carbon remaining unburnt in CFA. Generally, new types of pulverized coal boilers discharge lower LOI ashes less than 3%, while old types discharge higher ones exceeding 5%. In addition, general type fluidized bed boilers designed for high sulfur coal combustions discharge very high LOI ashes around 20%, exhibiting really black in color.¹⁵⁾

XRD charts of these two kinds of filler are represented in **Fig. 2**. The SSS was completely amorphous, while the CFA was not entirely amorphous, accompanied with small amounts of crystalline phases of quartz and mullite.

3.2 Flexural strength and bulk density

The physical properties of obtained hardened bodies are shown in **Fig. 3** in terms of CFA dosage, R. The bulk densities are proportional to the fly ash dosage, ranging from 1.81 to 1.56 g/cm³. That is, the more the fly ash, the lighter the bodies in specific weight. However, the flexural strength is not proportional to the dosage as have been encountered in a literature.¹⁶⁾ With increasing fly ash dosage the strength began to decrease up to around 50% dosage and turned up until the maximal 5.44 MPa was reached at 75% dosage. Then, it turned down again to 4.77 MPa of CAF only. The two extremes, SSS only CFA only, showed nearly the same strength despite of much difference of the bulk densities presumably due to the difference of specific surface

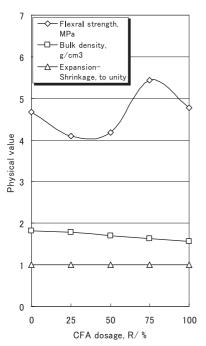


Fig. 3. Physical properties of solidified geopolymeric materials.

areas as well as the difference of dissolution natures between them. As a result, the present SSS was judged to be an active filler. Overall studies on the dissolution properties of sewage sludge slags are necessary henceforth as have been extensively studied on metakaolins and pyrophyllites as well as fly ashes, all of which are well-known active fillers.⁶⁾⁻⁸⁾

3.3 Expansion and shrinkage

In Fig. 3, expansion and shrinkage of obtained monolithic bodies are plotted in unity scale. When exceeding the unity, it means expansion and vice versa shrinkage. This property is proportional to the CFA dosage, R, starting from 1.000 to 0.9971. As a result, some contraction tendency was noted with increasing dosage of the CFA. The genuine SSS bodies showed little expansion and shrinkage, resulting exactly the mold size, while the bodies comprising the CFA showed a little shrinkage. According to literature,¹⁷⁾ the stable range is \pm 0.0004 from the unity. Therefore, present hardened bodies can be regarded stable in shapes, when the fillers consist of only the SSS. Although no cracking and bending have been encountered at the moment, the other mixes would have some risk in the long run.

This appreciably small shrinkage could be improved by introducing superplasticizers that can reduce the liquor amounts greatly, say down to ≈ 0.20 W/S from ≈ 0.40 W/S.¹⁸⁾ Press-forming will also do, which can reduce the liquor amounts. Therefore, the both techniques are useful not only for reducing binder liquor amounts but also for reducing binder costs. In case of Portland cement binders, only the required water are reduced in amounts. However, in case of geopolymer binders, not only the water but also the ingredients that are alkali-silicates as well as alkali activators are reduced together in amounts. A simple calculation indicates that the cost of present geopolymer binder is ≈ 1.8 times higher than that of Portland cement binders. This gap can be diminished down to half or less, say down to ≈ 0.9 times, which is as comparable as cement binders. In addition, the possible supplying amounts of sewage sludge slags are estimated to be insufficient at the moment due to the limited numbers of slag

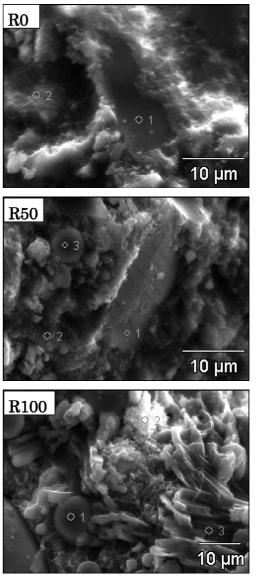


Fig. 4. SEM photomicrographs of solidified geopolymeric materials. RO (0%CFA), R50 (50%CFA) and R100 (100%CFA).

conversion plants. Therefore, blending sewage sludge slags with coal fly ashes has a high advantage in practical large scale productions of present geopolymeric materials.

3.4 SEM–EDX of fillers and matrices

An SEM photomicrograph of specimen debris designated R0 comprising only the SSS is represented in **Fig. 4**. The SSS exhibited dark glassy fragments in shapes surrounded by binder matrices having sponge-like textures peculiar to gel materials. No trace of crystalline phases could be identified by XRD of which chart was nearly the same with that of in Fig. 2 and was omitted here.

As seen in **Table 3**, spot 1, an SSS portion of specimen debris R0, showed chemical compositions similar to the bulk chemical compositions of the slag tabulated in Table 2, but the increasing SiO_2 component indicated considerably high dissolutions of other components. Spot 2 of a matrix portion showed different chemical compositions, where relatively high accumulations of CaO, MgO and P₂O₅ components were noted other than theoretically expected Al₂O₃ and SiO₂, associated with minor compo-

Table 3. SEM-EDX Results of Chemical Compositions for Obtained Geopolymeric Materials

Specim	nen	Spot	SiO_2	$TiO_2 \\$	$Al_2O_3\\$	Fe_2O_3	MnO	CaO	MgO	K_2O	Na ₂ O	SO_3	P_2O_5
R0	SSS	1	29.53	_	20.45	3.50	_	10.34	5.99	1.25	3.72	_	25.23
	Matrix	2	32.58	1.20	17.83	3.72	-	10.49	4.82	1.27	6.64	-	21.45
R50	SSS	1	42.65	_	20.51	2.12	_	6.07	2.36	1.39	9.86	_	15.05
	CFA	3	50.87	-	38.78	4.72	-	0.40	0.46	1.94	1.91	-	0.91
	Matrix	2	47.79	1.08	12.46	2.98	-	7.14	3.20	1.19	11.14	-	13.03
R100	CFA	1	70.74	0.71	19.54	3.12	_	_	0.84	2.77	2.28	_	_
	Matrix	2	52.69	0.41	12.91	2.13	-	1.51	0.44	0.85	21.90	7.16	_
R100	Extra	3	33.96	0.31	8.57	2.10	-	1.14	-	0.56	49.21	4.14	-
	phase	*	22.48	_	5.51	1.56	-	1.04	-	0.43	67.32	1.66	-
		*	23.15	0.40	7.25	1.79	-	1.27	-	0.63	60.07	5.43	-

* Photomicrographs are not shown in text. All analytical values are normalized to 100.

nents of TiO₂ and Fe₂O₃ as well as K₂O.

It should be bear in mind that the matrices were thoroughly composed of Na₂O and SiO₂ in the beginning. Moreover, the molar ratio between the Na₂O and the SiO₂ of present geopolymer liquor is nearly 1:1, corresponding to Na-metasilicate composition, Na₂O-SiO₂. This molar ratio is nearly identical even in weight ratio due to having nearly the same formula weight between Na₂O and SiO₂. Therefore, this 1:1 ratio is very much helpful to the qualitative discussions of dissolutions and incorporations mentioned here. Firstly, the incorporation other than Na₂O and SiO₂ components means occurring dissolutions from the fillers to yield polycondesed matrices during the hardening process of the specimen. Secondly, dissolution and incorporation trends can be estimated by comparing the EDX compositions against the XRF bulk compositions represented in Table 2 for corresponding fillers.

For the polycondensation of geopolymer liquors, it is postulated that dissolutions of Al_2O_3 and SiO_2 components dissolved from fillers play an important role. The analysis of spot 2 strongly supports this, but the role of CaO and P_2O_5 components is very high for the present polycondensation process. In addition, the role of MgO and Fe₂O₃ should be taken into account.

An SEM photomicrograph of a specimen debris comprising both of the SSS and the CFA by half and half in amounts, designated R50, is shown in Fig. 4. The two kinds of filler were clearly observed and the matrices exhibited the texture similar to the matrices of R0. By XRD no extra crystalline phases were identified other than quartz and mullite included in the CFA filler. Therefore, the matrices are composed of gel materials similar to R0 and the XRD chart was omitted here.

EDX results showed a remarkable enrichment of SiO₂ component for the SSS filler due to the result of marked dissolutions of CaO and P₂O₅ components from the SSS filler. On the other hand, some escapement of SiO₂ component was noted on the CFA filler in R50, spot 3, resulting a relatively high increase of Al₂O₃ component. Referring to the matrices, incorporation of CaO and P₂O₅ component was clearly noted other than Al₂O₃ and SiO₂ components.

An SEM photomicrograph of a specimen debris, designated R100, only comprising the CFA, is represented in Fig. 4. Relative enrichment of SiO₂ component was noted in R100, spot 1, presumably due to some escapement of Al₂O₃ component as well as CaO component as major dissolution components. To the contrary, matrices were mainly enriched with Al_2O_3 component in addition to SO_3 component as seen in R100, spot 2. Incorporation of CaO component is very minor, since the content of this component is minor in the original raw CFA filler. Incidentally, incorporations of Fe₂O₃ and MgO components were reported so far in the literature,¹⁹⁾ but incorporation of SO₃ component has not been detected so far, which was highly accumulated in the matrices presumably due to having high dissolution properties of SO₃ species from CFA fillers as to be mentioned below.

Although EDX analyses were performed on other spots of these three specimens, R0, R50 and R100, no great deviations were found in analytical values. Therefore, we believe that the discussions mentioned above are reliable enough.

It is noteworthy to mention about an extra crystalline phase encountered in R100 in present study. As seen in R100, spot 3, this crystalline material appeared in elongated hollow shapes. EDX results are represented in Table 3 together with other spots in different photomicrographs. This phase was characterized by high contents of Na₂O and SiO₂ associated with some Al₂O₃ and SO₃. CaO and Fe₂O₃ are in minor. Estimating from these results, this phase would be related to an alkali-silicate. According to the phase diagram of Na₂O-SiO₂, the phase most abundant in Na₂O is 2Na₂O·SiO₂. Although considerably large deviations are noted in the analytical values, Na₂O/SiO₂ molar ratio 2.1 can be obtained by averaging the obtained three spots, which is close to 2.0. On the other hand, however, this extra phase would not be a genuine 2Na₂O·SiO₂. The new phase is incorporated with the associated minor components and would have a certain range of compositions like solid solutions. This phase would be dissolved in the water trapped in the voids of hardened bodies in the oven conditions. When cooled down by taking out the mold from the oven after the end of steam curing, this phase might precipitate. The hollow structure supports this speculation, since this morphological structure forms in ultra high supersaturated conditions. These results strongly indicate that the associated components are also highly soluble to geopolymer liquors, specifically Al₂O₃ and SO₃ components. In addition, the dosage of the geopolymer liquor would be somewhat in excess of the adequate amounts in present preparation and this excess liquor mixing should be avoided, since this phase would not be so high resistant to water, estimating from the chemical compositions. We attempted to detect this new extra crystalline phase by XRD, but it was unsuccessful probably due to minor and local presence. Only quartz and mullite of the CFA origin were identified similar in Fig. 2. The matrices of R100 are also amorphous and the XRD chart was omitted here.

3.5 Supplements for the slag, SSS

Referring to the setting nature of the SSS is noteworthy. At room temperature, R0 mixtures showed very sluggish setting. Although the setting time is not yet been measured at the moment, it is more than 3 h. This slow setting is very much favorable to practical applications, since at least 1 h is necessary for casting large size products in practice. Metakaolin fillers show fast setting, when Na-silicate binders are applied together with NaOH solutions as activators. This problem is conquered by using K-silicate solutions together with KOH solutions as activators, but which are costly. Some researchers say blending KOH solutions in place of NaOH solutions is effective to prolong the setting time, even if Na-silicate solutions are used.²⁰⁾ Fly ash fillers generally show moderate setting, but some researches say they show sometimes very rapid setting less than 20 min, when geopolymer liquors consisting of Na-silicate and NaOH solutions are used. This phenomenon is also conquered by blending KOH solutions in place of NaOH solutions as activators. According to authors' experience, the setting time of CFA fillers is dependent on power plants, in other words, contents of lime component. In order to avoid the short setting time, low lime CFA are recommended to use.

Finally, referring to the SSS again, gradual shrinkage took place for R0 bodies, when cured at room temperature. As a consequence, around 3% linear contraction was encountered at 28 d age. Accordingly, room temperature curing is not suitable for SSS fillers. However, when the R0 mixtures are cast and warmed in the steam oven, rapid solidification takes place in 20 min. Accordingly, steam curing process is strongly recommended to obtain stable geopolymeric materials in dimensions. Incidentally, CFA fillers can be consolidated stable at room temperature, but it takes nearly 2 months. Therefore, steam conditions are also recommended for coal fly ashes.

4. Conclusion

In this study, following items have been drawn as conclusion. (1) The swage sludge slag, SSS is an active filler. At room temperature, however, solidification is very sluggish due to slow setting and it is hardly possible to obtain stable monolithic bodies in dimensions by way of room temperature curing. To conquer this problem, steam curing is required to obtain stable bodies in short period of time. Satisfactory results have been reached, when cured at 80°C.

(2) Mechanical strength of the monolithic bodies can be improved by blending the sewage sludge slag, SSS with the fly ash, CFA and the maximum is reached by 75% CFA blending, that is specimen R75.

(3) The above two items are very much useful to practical applications. Sufficient handling time is available for casting large size products to make use of the both properties, sluggish

solidification at room temperature and rapid solidification at elevated temperature around 80°C. According to the statistics, 18 slag conversion plants are working in the year of 2006 all over Japan. The output of the slag amounts for 36 thousand tons, which is insufficient to the practical productions of large scale such as acid resistant sewer pipes and so on. This issue can be supplemented by blending CFA fillers discharged enormous in Japan.

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