Preparation of monolithic geopolymer materials from urban waste incineration slags

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Urban waste incineration slags have been applied as active fillers of geopolymer. They are classified into two groups. One is Fe-rich and the other is Fe-poor in chemical compositions. When plotted in a ternary diagram in terms of CaO–Al2O3–SiO2, they aligned along with so-called the first hydraulic line and two groups were also noted. One is Ca-rich designated as BFS-group plotted near 45% CaO line close to blast furnace slag compositions. The other is Ca-poor designated as MID-group plotted near 30% CaO line apart from the blast furnace slag compositions. Na-silicate solution, Na2O·2SiO2·aq enriched with caustic soda was used as geopolymer liquor. When flooded, some foaming and swelling phenomena were encountered more or less presumably due to the degassing of hydrogen from contaminated Al-metal in the slags. When cured at 80°C and 100% RH, flexural strength tests for pastes revealed two groups of strength, very low and very high, ranging 3–16 MPa for 24 h curing, for instance. The strength was not depending on the iron contents but depending on the degrees of foaming and swelling, i.e., bulk densities of the hardened bodies. Sufficient work time for mixing and casting was able to take for all the slags even to the BFS-group. Matrix binder compositions of hardened pastes analyzed by SEM-EDX were discussed in terms of Al2O3/(Na2O + K2O), (CaO + MgO)/SiO2 and SiO2/Na2O as well as CaO–Al2O3–SiO2.

Key-words : Geopolymer, Slag, Incineration ash, Urban wastes, Water glass, Sodium silicates

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1. Introduction

Currently, so-called wastes are managed in three categories in Japan, i.e., industrial wastes, general wastes and radioactive wastes. Referring to non-radioactive wastes, nearly 400 million tons of industrial wastes and nearly 50 million tons of general wastes are discharged in Japan every year. As for the general wastes, mostly consisting of urban refuses, nearly 80% are burnable and incinerated so as to prevent foul-odor together with volume reduction to one-fifteenth to one-twentieth. As a consequence, 10 million tons remain as ash. To do further volume reduction for elongation of service life of final disposal sites, nearly 8% of the ash are converted into slags by smelting. Eventually, the volume shrinks to around one-thirtieth to one-fourth against raw wastes and 0.8 million tons of the slags come out every year. It is anticipated that this value becomes 1 million tons in 2014 due to shortage of disposal sites.1)

The ash contains hazardous dioxin and heavy metals as well as chlorine. Although most modern incineration plants working at higher temperature have facilities to disintegrate the dioxin, smelting process has an advantage of eliminating the dioxin as well. Oil fuels are generally used for the smelting, but most modern plants work with electricity thermo-generated in the incineration plants, in which heavy metals mostly consist of metallic iron sink to the bottom of the smelting chamber as mat so that slag portion floating on the mat can be taken out independently. Consequently, this type of slags is less contaminated with heavy metals than those of the oil smelting type. However, chlorine contamination cannot be avoided even by the electric smelting plants, since flying dust, also called fly ash, consisting of volatiles and particulates of incineration ash is mixed together with main ash.

There have been so far some techniques to apply water glasses as binders.2) Among them it was Davidovits who reinvestigated these binders as inorganic polymers from a chemical point of view.3–5) These new concept binders are classified into silicate polymers which are nowadays called “geopolymers” accepted by many researchers over the world. Readers are kindly requested to refer to the literatures for further knowledge of geopolymers.6–10)

Using geopolymer binders, so often called geopolymer cements or simply geopolymers, we can make products similar to those of Portland cements, namely pastes, mortars and concretes. Advantages of geopolymers are as follows:

1) Since geopolymer process is less dependent on virgin limestone, carbon dioxide emissions are reduced down to 65–80% in comparison with the Portland cement process.4,11)
2) High acid resistance racking to Portland cements. Therefore, application to sewage pipes has been attempted to aim long service life products.
3) High fire resistance durable to ~1000°C, exceeding Portland cement durable to ~400°C.
4) No alkali-silica reactions so that any kinds of aggregate can be used unlike Portland cements.
5) Much more wastes can be used than Portland cement process as raw materials so as to meet perfect zero-emission societies.
6) Less heat liberation during hardening so as to meet massive constructions such as dams.11)
7) In addition, it is said that geopolymer products have super
high lifetime of millennium order, but there are few studies on this subject.

On the other hand, geopolymers have some disadvantages as follows:

(1) Hardening principle is totally reverse to Portland cements, namely hydration for Portland cements, while dehydration for geopolymers due to polycondensation. Therefore, relatively high shrinkage is unavoidable for geopolymer products. Countermeasures are attempting at the moment, for instance, dosage of anti-shrinkage agents, raising pH of geopolymer liquor by adding alkali-hydroxides to the water glass liquor and so on.12) 13) Among them some dosage of fine coal fly ash such as JIS class I, over 5000 cm²/g Blaine, is now attracting attentions.14)

(2) Short period of work time for casting and molding is another issue. In case of metakaolin elongation of this period can be attained by applying K-based water glass added with K-hydroxide.3)–5) No countermeasures have been found for blast furnace slags having very short period of work time. In case of coal fly ash this disadvantage can be avoided by using so-called ASTM class F fly ash having low CaO, 1.3–4.1%. However, stable solidification of fly ash is very difficult at room temperature. Accordingly, as far as fly ash is concerned, applications of geopolymers are limited to so-called second products or precast products manufactured by steam curing. Recently, it has been found out that sewage sludge slags are suitable for the second products due to having sufficiently long period of work time.15)

For urban waste incineration ashes, which are generally inactive to alkaline solutions, there have been some studies.16)–18) However, for urban waste incineration slags, which are generally active to alkaline solutions, few studies have been found so far. In this paper, standing on what mentioned above, some urban waste incineration slags essentially consisting of CaO–Al₂O₃–SiO₂ as major components will be studied in order to apply them to second products of geopolymers.

2. Experimental

Some urban waste incineration slags, hereafter called U-slags in short, were collected from 5 smelting plants in western Japan, most of which is oil burner types as shown in Table 1. They were pulverized into powders by a laboratory pot mill and sieved under 63 μm to serve for active fillers. Their apparent densities and specific surface areas were measured by a specific gravity bottle and a Blaine apparatus, respectively. Chemical compositions were determined by the fluorescent X-ray technique, XRF, employing Philips MagixPro with FP method using pressed powder discs. Microstructures and crystalline phases of the fillers and resulting hardened bodies as well as matrix binder compositions were examined by the scanning electron microscopy equipped with the energy dispersive X-ray spectroscopy, SEM-EDX, and the X-ray diffractometry, XRD, employing Jeol JSM-6300F and Philips MPD1880, respectively.

A sodium type water glass designated as JIS No. 1 having approximately Na₂O–2SiO₂·aq composition was applied by diluting it to 1.27 specific gravity solution with deionized water. The hardening solution called “geopolymer liquor” was prepared by mixing this water glass solution with 10 M caustic soda solution in 3:1 proportion by volume to prevent shrinkage and then standing at least overnight before use. Incidentally, the composition of this liquor is corresponding to metasilicate composition, Na₂O·SiO₂·aq. Three-cell type molds were used having 20 × 20 × 80 mm prismatic dimension of each cell. Pastes were prepared by mixing the fillers with the geopolymer liquor in 0.40 liquor/filler ratio, L/F, corresponding to W/C or W/B of the Portland cement system. Pastes prepared by flooding and hand-mixing in a plastic beaker were cast into the molds and were kept standing for 1 h at room temperature prior to transferring to the oven and then steam-cured under 80°C-100% RH condition, holding for 3, 6, 12, 24 and 48 h, respectively. The raising time to reach the constant temperature was nearly 30 min. Samples were immediately taken out after finishing the curing time and demolded. Three-point flexural strength tests were performed after 1 day of the curing by employing a testing apparatus, Orientec Tensional RTC-1250A under the conditions of 50 mm span and 0.2 mm/min cross-head speed. Mean values of three test-pieces were taken as fracture loads, which were recalculated into flexural strengths according to the well-known formula, S=(3L/2bd²)p=kP where S, P and L are flexural strength, fracture load and span, respectively, and b and d are width and height of the cross section of each prismatic test-piece, respectively. The constant k becomes 9.375 × 10⁻⁴ in the present test. Bulk densities were obtained from the weight and volume of each test-piece prior to the fracture test.

Using debris, identification of mineral derivatives of hardened bodies as well as observation of fractured surface was conducted by XRD and SEM as mentioned. Matrix binder compositions that were hardened geopolymer liquor portions as binders surrounding the fillers remaining intact were determined by SEM-EDX using polished specimens of debris dried at 100°C overnight in an oven.

Pore size distributions were also measured by the mercury intrusion technique employing Quantachrome Pore Master 60GT using debris which were once heated at 100°C overnight and sieved and sorted between 2.38–5.66 mm in size.

Furthermore, laboratory scale work time was measured at room temperature. A small amount of pastes prepared with L/F 0.40 was filled in 30φ × 25 mm plastic vessels. Then, a Vicat needle was stuck to determine initial and final setting times. Finally, work time was estimated from penetrating patterns as to be mentioned.

3. Results and discussion

3.1 Physicochemical properties of U-slags

Physicochemical properties of present fillers prepared from as received U-slags are tabulated in Table 2. For chemical compositions two types are noted, namely Fe-poor and Fe-rich. The former is U1, U2 and U3 and the latter U4 and U5. The other peculiar point is low level chlorine contaminations originated to sodium chloride components included in foods and plastic appliances discarded from households.

For simplicity, the chemical compositions are plotted in a ternary phase diagram as shown in Fig. 1 in terms of CaO–Al₂O₃–SiO₂.19) It is obvious that the plotted points are located in low melting area of the phase diagram and align from U1 to U5 alongside with so-called the first hydraulic line comprising blast furnace slags and coal fly ashes. Two groups are noted as well. One is U1 and U2 of Ca-rich plotted close to the points of blast

Table 1. Outlined specifications of smelting plants of U-slags

<table>
<thead>
<tr>
<th>No.</th>
<th>Key</th>
<th>Operating temperature, °C</th>
<th>Smelting type of plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>U1</td>
<td>1350</td>
<td>Oil burners</td>
</tr>
<tr>
<td>2.</td>
<td>U2</td>
<td>1400</td>
<td>Oil burners</td>
</tr>
<tr>
<td>3.</td>
<td>U3</td>
<td>1500</td>
<td>Electric smelting</td>
</tr>
<tr>
<td>4.</td>
<td>U4</td>
<td>1300–1500</td>
<td>Oil burners</td>
</tr>
<tr>
<td>5.</td>
<td>U5</td>
<td>1250</td>
<td>Oil burners</td>
</tr>
</tbody>
</table>
The other is U3, U4 and U5 of Ca-poor plotted apart from the blast furnace slags. These two groups are designated as BFS-group and MID-group, respectively, hereafter for convenience.

XRD diagrams are represented in Fig. 2, indicating all the U-slags are almost entirely amorphous with a glassy hump centered at around $2\theta = 30^\circ$. However, a small amount of quartz peak was identified for U2 at around $2\theta = 26^\circ$. This quartz peak was also noted for U3, U4 and U5 in trace. Furthermore, a small amount of gehlenite peak was seen in U1 at around $2\theta = 32^\circ$. According to literature,20) gehlenite was identified as a stable phase in U-slags. The quartz included in urban wastes would remain undissolved and intact. Representative SEM images are in Fig. 3, revealing glassy fragments of the fillers consisting of sharp edges.

### 3.2 Work time at room temperature

Vicat needle penetration curves are shown in Fig. 4 as a function of time. It is obvious that hardening time is prolonged with decreasing CaO contents. BFS-group showed relatively fast hardening, while MID-group relatively slow hardening. An abrupt kink point appeared just before final setting was regarded as work time of laboratory scale in this study for convenience. That was 3, 5, 10, 16.5 and 20 h in the order of U1 to U5. In any case, sufficient work time was available. It is said that more than 1 h is desirable to mold large size products in practical applications to prevent a mixer choking from production line troubles to stop. Although how to determine the setting time has already been established so well, how to determine the work time has not been established yet even in academic societies. They say, for instance, the work time is the time to reach 2.5 cm slump in case of concretes made from regulated set cements.21) In case of geopolymer pastes a mixing spoon method is applied.11) These two methods consume much amount of samples.

### 3.3 Materials strength

No marked influence of iron-components on the strength was observed. As shown in Fig. 5 results of the flexural strength test can be classified into two groups. One is high strength group comprising U3, U1 and U5, and the other is low strength group comprising U2 and U4. It should be noted that when cast and molded, all the fillers showed foaming and swelling phenomena more or less due to presumable releasing of hydrogen gas from amphoteric Al-metal included in the U-slags, of which roots might be metallic Al-appliances such as cans and wrapping foils discarded from households as pointed out in literature.22) They used U-slags as fine aggregates of concretes and encountered so-called “pop-out phenomena” of hardened bodies due to delayed

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**Table 2. Physicochemical characteristics of U-slags**

<table>
<thead>
<tr>
<th>Major</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>SO$_3$</th>
<th>Total(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1</td>
<td>31.87</td>
<td>1.86</td>
<td>13.05</td>
<td>4.63</td>
<td>0.14</td>
<td>37.97</td>
<td>2.29</td>
<td>2.51</td>
<td>0.68</td>
<td>2.72</td>
<td>0.60</td>
<td>98.32</td>
</tr>
<tr>
<td>U2</td>
<td>33.29</td>
<td>1.61</td>
<td>13.77</td>
<td>5.23</td>
<td>0.16</td>
<td>33.72</td>
<td>2.65</td>
<td>1.68</td>
<td>0.76</td>
<td>4.26</td>
<td>0.64</td>
<td>97.77</td>
</tr>
<tr>
<td>U3</td>
<td>40.90</td>
<td>1.66</td>
<td>16.56</td>
<td>1.26</td>
<td>0.15</td>
<td>27.95</td>
<td>2.19</td>
<td>3.58</td>
<td>1.68</td>
<td>2.21</td>
<td>0.72</td>
<td>98.86</td>
</tr>
<tr>
<td>U4</td>
<td>38.47</td>
<td>1.74</td>
<td>13.89</td>
<td>10.72</td>
<td>0.23</td>
<td>23.32</td>
<td>2.33</td>
<td>3.46</td>
<td>1.48</td>
<td>1.93</td>
<td>0.15</td>
<td>97.72</td>
</tr>
<tr>
<td>U5</td>
<td>37.03</td>
<td>0.93</td>
<td>12.85</td>
<td>19.33</td>
<td>0.28</td>
<td>20.92</td>
<td>1.73</td>
<td>2.34</td>
<td>1.40</td>
<td>2.63</td>
<td>0.70</td>
<td>98.44</td>
</tr>
</tbody>
</table>

Total(1) = For major components Total(2) = For minor components omitted here App. = Apparent
degassing out of the aggregates. It is estimated that the Al-metal, which could not be identified by XRD due to very minor presence, is disseminated in very small domains in the glassy U-slags. Incidentally, metallic Al powders are applied to cellular materials of geopolymers as well as Portland cements as a degassing agent.

The degrees of foaming and swelling that reflect to bulk densities are strongly concerned with the strength. The high strength group, U3, U1 and U5 exceeding 10 MPa showed around 1.9 g/cm³, whereas the low strength group, U2 and U4 not exceeding 5 MPa showed around 1.3 g/cm³. It should be stressed that less foaming and swelling was observed for U3 presumably due to scares contamination of metallic Al, of which plant is an electric smelting type as mentioned. It should be stressed again that most of free metallic components sinks to the bottom of the smelting chamber as mat together with metallic iron that is a main portion of the mat. Accordingly, electric type smelting plants are superior to oil type ones in separation capability of metals out of U-slags. It is no doubt that the Al metal contaminations would be a problematic issue for recycling of U-slags, which might be strongly related to life styles of municipal residents, more dependent on or less dependent on Al-metal appliances.

Referring to 3 h strength, U1 and U2 both belonging to BFS-group could be demolded safe at this age presumably due to higher CaO contents as mentioned. It can be said that all present fillers are classified into active filler family but a heating process by steam is required to obtain stable and strong monolithic bodies.

3.4 SEM observation of hardened bodies

Exemplified SEM images are shown in Fig. 6 for 24 h cured bodies. Considerably large degassing holes can be seen in U2 which showed low strength due to low bulk densities. The same is true for U4. To the contrary, frequency of the holes becomes less for U3 which showed highest strength in this study due to high bulk densities. The same is true for U1 and U5. It should be stressed that degassing holes are seen even in U3 of which slag was discharged from an electric smelting plant having high capacity of free metal exclusion.

3.5 XRD of hardened bodies

XRD diagrams are represented in Fig. 7 for 24 h cured specimens. Three main features could be recognized. The first is the glassy humps centered at around $\theta = 30^\circ$, originated to remaining U-slag fillers. The second is calcite peaks of which characteristic peaks are located at around $\theta = 30^\circ$. The third is a peak characteristic to quartz noted to U2 at around $\theta = 26^\circ$ other than calcite peaks. When compared to Fig. 2 of raw fillers, this quartz peak was diminished in other specimens, presumably due to some reactions of quartz occurring in alkaline circumstances during steam curing. The same is true for the minor gehlenite peak in U2. No mineral peaks were identified to U5 of which filler contains much amount of iron-component as shown in Table 2. Nevertheless, some very minor peaks remained unidentified throughout all the specimens.

The calcite might form from portlandite carbonation, which might form from free lime, CaO, presumably presented in the raw U-slags in minor. Much iron contents might suppress the free lime formation due to effective lowering of melting points of U-slags.
3.6 Pore size distributions of hardened bodies

Representative pore size distributions for 24 h cured specimens are in Fig. 8, which are characterized by two prevailing peak groups, larger size pores and smaller size pores bounded by 1 μm. The larger size pores are seen at around 10–100 μm, which would originate to the degassing, since U2 and U4 swelled so much exhibiting enhanced frequencies on this peak region. To the contrary, high density specimens, U1, U3, U5 showed decreased frequencies in this region and minimum was reached by U3 swelled scars. However, this peak region was missing for U5 of iron-rich showing medium frequency at around 1 μm.

The smaller size pores are seen at around 0.01–0.1 μm, which would originate to geopolymer binders themselves which generally exhibit sponge-like textures due to amorphous gel characters. U1, U3, U4 and U5 showed enhanced frequencies and U2 showed decreased one. Referring to the peaks centered at around 0.01 μm, U5 has highest frequencies, which might have high capability as indoor humid regulation materials that require extremely small pores obeying the Kelvin’s sorption and desorption equation of capillaries.24)

3.7 SEM-EDX analyses of matrix binders

Results are tabulated in Table 3 in molar for 24 h cured specimens. Two reliable spots are picked up from several analytical spots, which are designated as M1 and M2 for each specimen. The criteria of selection were more Na-contents for matrix binders in order to exclude the influences from tailing sized fillers being extremely fine. Generally, the matrix binders showed nearly similar chemical compositions within each specimen. However, U5 rich in iron showed much fluctuated compositions presumably due to inhomogeneous nature of matrix binders. The same is true for U2. At a glance, clear incorporations of Al₂O₃ and CaO were noted as major components other than SiO₂. Furthermore, considerably large incorporations of Fe₂O₃ were found specifically in iron-rich specimens, U4 and U5. Iron incorporations have already been pointed out in literature.13)

It should be mentioned that a considerably large number of the SiO₂-component might dissolve from the mother fillers into matrix binders. Present raw geopolymer liquor has equi-molar ratio, SiO₂/Na₂O = 1, corresponding to metasilicate composition. Analyzed results showed that a quite large number of silica enrichment took place in matrix binders, giving rise to enhanced molar ratios of 4.51 to 7.58 from unity. Silica dissolution has already been elucidated in some literatures for metakaolins and pyrophyllites as well as fly ashes, using alkaline solutions.25)–27)

It seems likely that Al₂O₃-components vary in harmony with Na₂O-components, showing the well-known replacement of Si⁴⁺ with Al³⁺ + Na⁺ and Al³⁺ + K⁺ as elucidated in synthetic gels formed in highly basic conditions.28),29) To make clear this
The alkaline earth was decreased with increasing silica ranging along the negative correlation as seen in Fig. 10 and in normal type N–A–S–H (CaO–Al2O3–SiO2–H2O) gels other than normal type N–A–S–H(N = Na2O) and C–S–H gels was suggested in literature studied by FTIR and SEM-EDX in a metakaolin-alumino-cement system activated with SM caustic soda solution.31) The binder gel compositions discussed above might become an important issue from now on in the course of studying geopolymers.

Table 3. SEM-EDX spot analytical data of matrix binders in molar for pastes steam-cured for 24 h

<table>
<thead>
<tr>
<th>SiO2</th>
<th>TiO2</th>
<th>Al2O3</th>
<th>Fe2O3</th>
<th>CaO</th>
<th>MgO</th>
<th>Na2O</th>
<th>K2O</th>
<th>P2O5</th>
<th>SO3</th>
<th>S/N</th>
<th>(C + M)/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>U1-M1</td>
<td>47.02</td>
<td>0.72</td>
<td>7.42</td>
<td>1.30</td>
<td>32.73</td>
<td>1.69</td>
<td>7.65</td>
<td>0.45</td>
<td>0.12</td>
<td>0.91</td>
<td>6.15</td>
</tr>
<tr>
<td>U1-M2</td>
<td>45.54</td>
<td>0.71</td>
<td>7.15</td>
<td>1.33</td>
<td>34.16</td>
<td>1.89</td>
<td>7.75</td>
<td>0.36</td>
<td>0.11</td>
<td>1.01</td>
<td>5.88</td>
</tr>
<tr>
<td>U2-M1</td>
<td>50.62</td>
<td>1.00</td>
<td>8.84</td>
<td>1.52</td>
<td>22.26</td>
<td>3.64</td>
<td>9.73</td>
<td>0.44</td>
<td>0.89</td>
<td>1.06</td>
<td>5.20</td>
</tr>
<tr>
<td>U2-M2</td>
<td>58.78</td>
<td>1.00</td>
<td>10.11</td>
<td>1.42</td>
<td>15.38</td>
<td>2.40</td>
<td>8.64</td>
<td>0.62</td>
<td>0.38</td>
<td>1.26</td>
<td>6.80</td>
</tr>
<tr>
<td>U3-M1</td>
<td>49.07</td>
<td>0.98</td>
<td>7.93</td>
<td>0.39</td>
<td>29.18</td>
<td>2.54</td>
<td>7.69</td>
<td>0.82</td>
<td>0.12</td>
<td>1.28</td>
<td>6.38</td>
</tr>
<tr>
<td>U3-M2</td>
<td>51.17</td>
<td>0.99</td>
<td>8.48</td>
<td>0.58</td>
<td>26.99</td>
<td>2.55</td>
<td>7.10</td>
<td>0.92</td>
<td>0.07</td>
<td>1.16</td>
<td>7.21</td>
</tr>
<tr>
<td>U4-M1</td>
<td>55.25</td>
<td>1.37</td>
<td>9.23</td>
<td>4.23</td>
<td>13.87</td>
<td>4.10</td>
<td>9.48</td>
<td>1.01</td>
<td>1.14</td>
<td>0.31</td>
<td>5.83</td>
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<tr>
<td>U4-M2</td>
<td>53.64</td>
<td>1.32</td>
<td>8.54</td>
<td>3.93</td>
<td>13.98</td>
<td>4.51</td>
<td>11.89</td>
<td>1.12</td>
<td>0.92</td>
<td>0.17</td>
<td>4.51</td>
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<tr>
<td>U5-M1</td>
<td>51.69</td>
<td>0.65</td>
<td>8.03</td>
<td>0.73</td>
<td>21.28</td>
<td>6.82</td>
<td>0.76</td>
<td>0.59</td>
<td>0.32</td>
<td>7.58</td>
<td>0.47</td>
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<td>U5-M2</td>
<td>60.83</td>
<td>0.84</td>
<td>8.28</td>
<td>10.18</td>
<td>6.51</td>
<td>1.97</td>
<td>9.11</td>
<td>1.40</td>
<td>0.25</td>
<td>0.64</td>
<td>6.68</td>
</tr>
</tbody>
</table>

Normalized to 100 mole % MnO omitted due to very minor N = Na2O, C = CaO, M = MgO, S = SiO2.

Fig. 9. Relationship between alkalis and alumina for matrix binders of pastes steam-cured for 24 h. For the arrow refer to the text.

Fig. 10. Relationship between silica and lime combined with magnesia for matrix binders of pastes steam-cured for 24 h.
Fig. 11. Linear alignment of matrix binder compositions of pastes steam-cured for 24 h in terms of CaO–Al₂O₃–SiO₂. Filler compositions of Fig. 1 are also plotted in mole % with large solid circles labeled U1 to U5 for comparison. Splitting pairs of M1 and M2 for U2 and U5 are tied, respectively. Refer to the text for further details.

4. Conclusion

Five varieties of U-slags have been investigated by pulverizing the slags to prepare fillers, which were solidified with the geopolymer binder under steam-curing conditions, 80°C-100% RH. Following items were drawn as conclusion:

(1) In view of chemical compositions two groups of fillers are found. One is so-called BFS-group having chemical compositions similar to those of blast furnace slags, and the other is so-called MID-group having lower CaO contents than those of blast furnace slags. When plotted in a ternary diagram in terms of CaO–Al₂O₃–SiO₂, all aligns alongside with so-called the first hydraulic line.

(2) When flooded and cast, degassing phenomena are observed more or less for all the fillers, presumably due to the presence of amphoteric Al-metal contaminated in the U-slags. Consequently, materials strength is dependent on the bulk densities of obtained geopolymer monoliths. Pore size distribution measurements show two distinct peak groups at around 0.01–0.1 μm and 10–100 μm. Both peak groups are enhanced for low density monoliths, while the latter peak group is almost diminished for high density monoliths.

(3) Although hardening properties of all the fillers are relatively slow and sluggish and no high strength solidifications are observed at room temperature. However, when steam-cured under 80°C-100% RH conditions, high strength monoliths are so easily obtained, if the Al-metal contamination is less, showing up to 16 MPa in flexural strength. In this respect, all the present fillers are classified into so-called the active filler. No difficulty is encountered in mixing and casting so that sufficient durations of work time are available. No marked influence of iron-contents of the U-slags is detected on strength so that the resultant materials strength is independent of iron contents.

(4) Present U-slags are amorphous due to glassy characters. Nevertheless, very minor presence of quartz as well as gehlenite is detected for some U-slags by XRD. After hardening some formation of calcite was also detected by XRD. This calcite formation is not observed for US being very rich in iron components.

(5) For matrix binders, a nearly linear relationship is observed on Al₂O₃ versus Na₂O + K₂O until 10 mole% Na₂O + K₂O are reached by SEM-EDX. Over 10 mole %, a ceiling increase of Al₂O₃ is observed, which might be canceled by supposed Fe₂O₃ incorporations. On the other hand, a negative linear correlation is observed in CaO + MgO versus SiO₂ in molar. The CaO + MgO components decrease with increasing SiO₂ until 8.48 mole% CaO + MgO are reached despite much CaO contents of the mother fillers. Marked dissolution and resultant incorporation of SiO₂ into matrix binders are also noted accompanied with SiO₂/Na₂O molar ratio enhancement to 4.51–7.58 from unity of starting geopolymer liquor, depending on specimens. As a consequence, matrix binder compositions shift from corresponding mother filler compositions to silica-rich directions in CaO–Al₂O₃–SiO₂ ternary plots, aligning almost straight.

References