Development of Low-Activation Design Method for Reduction of Radioactive Waste Below Clearance Level (7)

– Application of High Alumina Cement for Low-Activation mortar –

Ryoetsu Yoshino1, Taichi Mori1, Akira Hasegawa2, Masaharu Kinno3, Mikio Uematsu4, Katsumi Hayashi5 and Mikihiro Nakata6

1) Inorganic Material Research Center, Denki Kagaku Kogyo Kabushiki Kaisha, Niigata, Japan
2) Tohoku University, Sendai, Japan
3) Fujita Corp., Tokyo, Japan
4) Toshiba Corp., Yokohama, Japan
5) Hitachi Ltd., Hitachi, Japan
6) Mitsubishi Heavy Industries, Kobe, Japan

ABSTRACT

We have been developing the low-activation materials to reduce the costs of processing, managing and disposing wastes. High alumina cement, which was considered as favorable low-activation material because of its low content of cobalt and europium, was found to have problems of poor workability, high heat of hydration and long-term compressive strength reduction owing to the conversion. We investigated low-activation mortar with siliceous materials such as silica fume or fused silica for solving these problems. The mortars with fused silica could not improve the poor workability and high heat of hydration. Therefore, we developed calcium aluminate silicate glass additive. This additive was able to improve the quality of high alumina cement mortars. The suppression of reduction in long-term compressive strength, the improvement of workability and reduction of hydration heat at setting were achieved by applying this additive. The developed additive was confirmed to be an excellent low-activation material.

Introduction

Some shield concrete, steels and pipes around a reactor become low level radioactive waste at decommission phase because they contain radioactive nuclide. We have been developing the low-activation materials to reduce the costs of processing, managing and disposing wastes by using low-activation materials for construction.

High alumina cement (HAC) was found out about having excellent low-activation performance[1],[2],[3],[4]. Application of HAC for Reactor Shielding Wall (RSW) of a Boiling Water Reactor (BWR) and for Primary Shielding Wall (PSW) of a Pressurized Water Reactor (PWR) are expecting for reducing activation level of the shielding wall.

HAC is the successful special cement except for Portland cement. It has unique properties such as high early strength development behavior and strong chemical resistance. Especially, it has widely used for castable refractory because of high temperature resistance. On the other hand, HAC has not used for general structural purposes. Because it has higher cost than Portland cement and the ‘conversion’. The conversion of HAC sometimes causes serious reduction in long-term strength of hardened mortar or concrete. This phenomenon is caused from transformation the metastable phase to the stable one in calcium aluminate hydrates. Accordingly, it is necessary to solve the problem such as long-term durability when HAC is applied for low-activation mortar. Furthermore, a investigation about the properties of HAC such as workability in fresh mortar and crack at early age due to the high heat of hydration was needed for applying for this purpose.

This study reports the results of investigation about the application of HAC for low-activation mortar.

High alumina cement for low-activation material

The physical properties of HAC mortars were investigated on the assumption that it would be applied for RSW. It is well known that the physical properties of HAC mortars are affected with water to cement (W/C) ratio. First, we investigated the effect of W/C ratios on HAC mortars. The mortar specimens were prepared by the similar way to JIS R 5201, physical testing methods for cement. The mix proportion was adopted 25wt% HAC and 75wt% silica sand. And W/C ratios were applied 30%, 40% and 50%. HAC used for this study was DENKA High Alumina Cement Hi grade (Al2O3 74.0 wt%, CaO 24.7 wt%). The mortars of 30% W/C ratio were also used superplasticizer (polycarboxylate type) to obtain good workability at molding. The mortar bars of dimensions 40 x 40 x 160 mm were used. After de-molds(24hr.), the specimens were covered with aluminum foil and cured into the air at various temperature, 5, 20, 40, 65 °C. The compressive strength of these mortars were measured by JIS R 5201 and length change rates were measured using a dial gage.

Fig. 1 shows the compressive strength of the mortars. The compressive strength of the mortars cured at 5 or 20 °C were increased with time. And the strength was increased with decreasing W/C ratios. On the other hand, at 40 or 65 °C the strength of the mortars which W/C ratios were 40 % and 50% were rapidly decreased from initial strength. These reduction were caused by the conversion of hydrates. In contrast, the decrease of strength with W/C 30% mortar was
lower than the other W/C mortars. In addition, W/C 30% mortars had very high compressive strengths for all time.

Fig. 1 Compressive strength of HAC mortars at various cured temperature.

Fig. 2 shows length changes of the specimens. The length changes were also affected by W/C ratios. At 5 and 20 °C, the lower W/C mortars had lower shrinkage than higher W/C mortars. On the other hand, the shrinkage of the mortars which W/C ratio was 50% at 40 and 65 °C were lower than the other mortars.

Fig. 2 Length change of HAC mortars at the various cured temperature.
It is necessary for the realization of low-activation mortar to ensure the durability of HAC mortars. From the durability of HAC mortars, the reduction in compressive strength at high temperature had to be prevented. So, we investigated the physical properties of mortars with and without silica fume known to have the prevention effect against the conversion. Fig.3 shows the compressive strength of these mortars. The addition of silica fume produced good results. The mortars with 30% silica fume didn’t occur the conversion.

Fig.3  Compressive strength of mortars with and without silica fume (W/C 40%)

We investigated the impurities of silica fume for low-activation materials. Table 1 shows the impurities of the samples measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES, SII NanoTechnology Inc. Vista-PRO). The major target elements which decide the radioactivity level of disposal mortars were cobalt (Co) and europium (Eu). So, low-activation mortar was able to be manufactured by adequate selection of silica fume which had low Co and Eu contents. But, it was hard for selection to obtain the silica fume which invariably had low impurities content. On the contrary, fused silica had lower impurities level than silica fume. Then we adopted fused silica for the materials to prevent the conversion.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>country</th>
<th>content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>1</td>
<td>silica fume</td>
<td>Norway</td>
<td>0.28</td>
</tr>
<tr>
<td>2</td>
<td>China</td>
<td></td>
<td>5.3</td>
</tr>
<tr>
<td>3</td>
<td>China</td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>Australia</td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>fused silica</td>
<td>Japan</td>
<td>1.6</td>
</tr>
<tr>
<td>6</td>
<td>Japan</td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>7</td>
<td>Japan</td>
<td></td>
<td>1.1</td>
</tr>
<tr>
<td>8</td>
<td>India</td>
<td></td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>9</td>
<td>HAC</td>
<td>Japan</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td></td>
<td>lower limit of determination</td>
<td></td>
<td>0.20</td>
</tr>
</tbody>
</table>

For the purpose of ensuring the stable physical property, we investigated the characters of mortars which had lower W/C ratio with fused silica. Table 2 shows the mix proportion of mortar specimens. Table 2 includes the mortars which have been using heavy mortar for RSW. Compressive strength of these mortars and temperature raise at early stage were measured. Temperature curves of mortars at early stage were measured with thermo-couple into a vacuum bottle whose capacity was 1 dm$^3$.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Water/Binder ratio (%)</th>
<th>designed density (kg/m$^3$)</th>
<th>Unit content (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>water</td>
<td>HAC</td>
<td>fused silica</td>
</tr>
<tr>
<td>No.1</td>
<td>30</td>
<td>2.76</td>
<td>251</td>
</tr>
<tr>
<td>No.2</td>
<td>30</td>
<td>2.94</td>
<td>203</td>
</tr>
<tr>
<td>Present mortar for RSW</td>
<td>42</td>
<td>2.39</td>
<td>254</td>
</tr>
</tbody>
</table>
Fig. 4 shows compressive strength of the mortars cured at 40 °C. The both mortars with fused silica had very high compressive strength and no reduction in strength with the conversion. Fig. 5 shows the temperature curves of these mortars at early stage. The high heat of hydration may cause a crack in hardened mortar. No.1 mortar had high heat level and No.2 mortar had lower level than No.1. But, the heat of hydration of both mortars were higher than the one of present mortar for RSW. So, we needed to develop lower heat cement.

Photo.1 shows the flow states of these mortars. The present heavy mortar for RSW had good fluidity (Photo.1 (a)). On the other hand, No. 2 mortar had thixotropy (Photo.1 (b)). The thixotropy causes poor workability on fresh mortar or concrete. Then we increased the superplasticizer to obtain good fluidity (Photo.1 (c)). When the mortar had much superplasticize, the material separation was occurred (Photo.1 (C)). Consequently, it was necessary to develop the cement which had good fluidity.

Development of additive for low activation material

We developed the new cement additive for low-activation mortar and concrete. The targets of this development are as follows;

- Inhibitor to the conversion
- Improvement of fluidity on HAC mortar and concrete
- Decreasing heat of hydration at early stage
- Less Co and Eu contents

Calcium aluminate silicate glass material had excellent performance for these purposes. The new additive was made by electric furnace. The raw materials were used Lime, Silica stone and alumina with low impurities. Table 3 shows the characters of this additive and typical HAC.

Photo.2 shows the flow state of the mortar included 70% additive. This mortar had good fluidity and no thixotropy. And the mortar needed a small quantity of superplasticizer.
### Table 3 Characters of new additive and HAC

<table>
<thead>
<tr>
<th>Character</th>
<th>New additive</th>
<th>HAC (typical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main compound</td>
<td>calcium aluminate silicate glass</td>
<td>calcium aluminate</td>
</tr>
<tr>
<td>Basicity ((=\frac{\text{CaO}+\text{MgO}+\text{Al}_2\text{O}_3}{\text{SiO}_2}))</td>
<td>2.03</td>
<td>-</td>
</tr>
<tr>
<td>Density ((\text{g/cm}^3))</td>
<td>2.98</td>
<td>3.13</td>
</tr>
<tr>
<td>Blaine specific surface area ((\text{cm}^2/\text{g}))</td>
<td>6500</td>
<td>4800</td>
</tr>
<tr>
<td>Eu content ((\text{ppm}))</td>
<td>0.07</td>
<td>0.01 – 0.07</td>
</tr>
<tr>
<td>Co content ((\text{ppm}))</td>
<td>0.12</td>
<td>0.1 – 0.4</td>
</tr>
</tbody>
</table>

**Photo.2** Flow state of the HAC mortar included 70% new additive.

Fig.6 shows the compressive strength of the mortars. The compressive strength of the mortar with 70% new additive was the same level as the one of ordinary Portland cement without the conversion. Fig. 7 shows the temperature curves of the mortars at early stage. New Additive could achieve decreasing the heat of hydration at early stage.

**Fig.6** Compressive strength of mortars (W/C 40%, 40°C).

**Fig.7** Temperature curves of test mortars.

**Fig.8** Co and Eu contents of various materials measured by radioactivation analysis. New additive had lower impurities and excellent low-activation ability. Therefore, this additive had the excellent performances for low-activation materials.

**Fig.8** Co-Eu content map for various materials.
Hydration mechanism of HAC paste with new additive

We also analyzed the hydration HAC pastes with new additive. Fig. 9 shows X-Ray Diffraction (XRD) intensity curves of minerals in pastes cured at 40 °C. The paste with new additive had Stratlingite (2CaO.Al$_2$O$_3$.SiO$_2$.8H$_2$O). Stratlingite is known as a stable mineral in calcium aluminate hydrates. On the other hand, HAC pastes did not have stratlingite. The major hydrate phase was Tricalcium Aluminate Hexahydrate (3CaO.Al$_2$O$_3$.6H$_2$O) that was generated from other calcium aluminate hydrates (CaO.Al$_2$O$_3$.10H$_2$O, 2CaO.Al$_2$O$_3$.8H$_2$O, etc.) with the conversion. The pastes that were occurred the conversion had the structural defects of pore. Therefore, the deterioration of HAC products with strength drop was occurred because of increasing the defects. New additive achieved suppression of the conversion.

CA : CaO.Al$_2$O$_3$, CAH10 : CaO.Al$_2$O$_3$.10H$_2$O, C3AH6 : 3CaO.Al$_2$O$_3$.6H$_2$O, C3ASH4 : 3CaO.Al$_2$O$_3$.SiO$_2$.4H$_2$O, C2ASH8 : 2CaO.Al$_2$O$_3$.SiO$_2$.8H$_2$O, AH3 : Al(OH)$_3$

Fig. 9  XRD results of HAC pastes with and without new additive.(40°C)

However, shrinkage level of the mortar with new additive was higher than the one using ordinary portland cement (Fig. 10). It was necessary to improve the shrinkage of mortar with new additive.

Conclusion

We investigated application of high alumina cement for low-activation mortar. High alumina cement had excellent low-activation ability due to lower Co and Eu contents. However, the mortar that high alumina cement was applied was occurred reduction in long-term compressive strength. And the mortar also had the problems such as poor workability and high heat of hydration.

The reduction in long-term compressive strength was able to avoid by adding siliceous materials such as fused silica and lowering water to cement ratio. However, these mortars had poor workability and high heat of hydration.

We developed calcium aluminate silicate glass additive. This additive was able to improve the quality of high alumina cement mortars. The suppression of reduction in long-term compressive strength, the improvement of workability in
fresh mortar and the decrease of hydration heat at setting were achieved by this additive. And this additive also had excellent low-activation ability with low Co and Eu content.

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References