Development of Dusting Prevention Stabilizer for Stainless Steel Slag

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Synopsis:
Stainless steel slag with a basicity of over 1.5 pulverized into fine particles during cooling in the past. Such pulverization was liable to cause environmental problems and disturbed further utilization of slag. To solve such problems, a stabilizing agent has been developed which can prevent pulverization of the slag with only 0.5% addition. Borate is used as a stabilizer, and the content of its crystal water is adjusted to obtain more homogeneous diffusion and resolution in molten slag. Best result is achieved for K-BOP slag at 7% crystal water content, and the stabilized stainless steel slag after 3 months aging period becomes equivalent to blast furnace slag in its quality, thereby making it applicable to aggregate for road construction.

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Stainless steel slag with a basicity of over 1.5 pulverized into fine particles during cooling in the past. Such pulverization was liable to cause environmental problems and disturbed further utilization of slag. To solve such problems, a stabilizing agent has been developed which can prevent pulverization of the slag with only 0.3% addition. Borate is used as a stabilizer, and the content of its crystal water is adjusted to obtain more homogenous diffusion and resolution in molten slag.

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1 Introduction
Stainless steel slag disintegrates into a powdery state during cooling due to transformation of $2\text{CaO} \cdot \text{SiO}_2$, thereby not only causing environmental deterioration in the slag cooling yard, but also reducing the utilization scope of the slag. Prevention of such disintegration has been the major issue in stainless steel slag processing for a considerable time.

Conceivable methods for preventing this disintegration or dusting of slag include adding SiO$_2$ to the slag to produce CaO · SiO$_2$ and adding an additive to prevent crystal transformation of $2\text{CaO} \cdot \text{SiO}_2$. The former method requires a great deal of SiO$_2$ additive. The latter is not a method of adjusting the composition of slag, and therefore can be effective with only small additions of an additive to control transformation. Since addition of the additive in only small amounts permits its effective dissolution into slag, the latter method has been adopted. A stabilizer for prevention of slag disintegration has been developed with sufficient diffusibility in molten slag and is effective in an amount of only 0.5 wt% of the slag.

2 Dusting of Slag
The mineral composition of stainless steel slag after dusting during cooling is mainly $\gamma$-$\text{CaO} \cdot \text{SiO}_2$. Correlation exists between slag dusting and basicity. As shown in Fig. 1, dusting begins to occur at a basicity of about 1.4, and when basicity exceeds 1.55, slag completely disintegrates into fine particles. If the mole fraction of CaO · SiO$_2$ in the slag composition approaches 2 : 1, the $2\text{CaO} \cdot \text{SiO}_2$ quantity seems to increase.

Phases of $2\text{CaO} \cdot \text{SiO}_2$ are known to be types $\alpha$, $\alpha'$, $\beta$, and $\gamma$, and the relation between transformation sequence and transformation temperature is as shown below.

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Ionic radius of $B^{2+}$, $P^{3+}$ and $Si^{4+}$ in 4-coordinations:

\[ B^{2+}, \quad P^{3+}, \quad Si^{4+} \]

\[ 0.22 < 0.33 < 0.4 \text{ Å} \]

Ionic radius of $Ba^{2+}$, $Sr^{2+}$ and $Ca^{2+}$ in 6-coordination:

\[ Ba^{2+}, \quad Sr^{2+}, \quad Ca^{2+} \]

\[ 1.36 > 1.16 > 0.99 \text{ Å} \]

(3) Addition of 5% Fe$_2$O$_3$ to form type $\beta$. However, iron oxide may change its valence number under various conditions, and one theory maintains that FeO promotes the occurrence of type $\gamma$.  

(4) Additions of Al and Mo to wrap 2CaO·SiO$_2$ with aluminate or molybdate to form type $\beta$.  

(5) Reduction in crystalline particle sizes by rapid cooling from high temperature without using additives to form type $\beta$.

Ordinarily, transformation occurs in the sequence of “type $\alpha$ → type $\alpha' → type \gamma$,” but it is known that under certain conditions transformation progresses in the sequence of “type $\alpha' → type \beta$.” Density values for the respective types are:

- 3.07 for type $\alpha$
- 3.31 for type $\alpha'$
- 3.28 for type $\beta$
- 2.97 for type $\gamma$.

Transformation from type $\alpha$ to type $\alpha'$ poses no problems from the viewpoint of disintegration, because the transformation occurs in the molten slag, but transformation from type $\alpha'$ to type $\gamma$ is accompanied by volumetric expansion as great as about 14%.  

The prevention of dusting is to cause the slag to assume the composition $CaO·SiO_2$ instead of 2CaO·SiO$_2$; for this purpose, it is necessary to add about 20% SiO$_2$. However, it is ex-

3 Prevention of Dusting

The transformation from type $\alpha'$ to type $\beta$ has almost no volumetric expansion, so dusting can be prevented simply by promoting the transformation of type $\alpha'$ to type $\beta$. In connection with transformation from type $\alpha'$ to type $\beta$, prevention of dusting has been a topic studied by many researchers in the field of inorganic chemistry, and various methods have been proposed as follows:

(1) Substitution for $Si^{4+}$ of an ion having an ionic radius smaller than that of the $Si^{4+}$, or substitution for $Ca^{2+}$ of an ion having an ionic radius greater than that of $Ca^{2+}$.

(2) Substitution of ions having $C/R$ (valence/ionic radius) ratio smaller than 2 or greater than 9.5.

Fig. 1 Relation between stainless steel slag basicity and dusting ratio (dusting ratio (% means proportion of ~5 μm particles after cooling)

Liquid phase  \[\begin{array}{c}
2130°C \\
\rightarrow type \alpha \\
1450°C \\
\rightarrow type \alpha' \\
850°C \\
\rightarrow type \gamma \\
675°C \\
\rightarrow type \beta \\
\end{array}\]

Fig. 2 Comparison of borate with phosphate for stabilization of slag.
Table 1 Chemical composition of B.O.F. and K-BOP slag

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>BOF slag</th>
<th>K-BOP slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>40-50</td>
<td>48-54</td>
</tr>
<tr>
<td>SiO₂</td>
<td>10-15</td>
<td>32-33</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>2-5</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>2-9</td>
<td>10-11</td>
</tr>
<tr>
<td>Fe</td>
<td>15-20</td>
<td>0.7-0.9</td>
</tr>
</tbody>
</table>

Mineral composition

| 2CaO·SiO₂, MgO, Fe₀₂ | 2CaO·SiO₂, MgO, Fe₀₂ |

Phase 2: CaO·SiO₂·P₂O₅·F
Phase 3: MgO·Fe

Further, a detailed analysis of line A-A' in the SE image in Photo 1 is shown in Fig. 3. From the photos and the line analysis, the following was found:

1. The mineral composition of 2CaO·SiO₂ is equivalent to Phase 1; its particle size is 20 to 40 μm.
2. At the 2CaO·SiO₂ particle boundary, F, which seems to be fluorapatite, exists, indicating Phase 2

4 Role of Stabilizer in Slag

The action of the stabilizer on 2CaO·SiO₂ in the slag was investigated by EPMA. Since only a very small quantity of boron was added to the slag, and its characteristic X-rays intensity is weak, its distribution map was unclear. Hence phosphorous, which performs the same function, was used in the investigation. The results of EPMA observation of stainless steel slag stabilized by phosphate are shown in Photo 1. In view of the distribution maps, the mineral composition was broadly divided into the following three phases.

Phase 1: CaO·SiO₂·P₂O₅

Fig. 3 Analysis of A-A' line in Photo 1

Photo 1 Photograph and EPMA X-ray area for elements in stabilized slag
mineral composition.

(3) P exists in 2CaO·SiO₂ as solid-solution of 1 to 1.5% P₂O₅, and excess P₂O₅ is pushed to the particle boundary.

From the distribution map of P₂O₅, it is inferred that B₂O₃ is also contained in 2CaO·SiO₂ as solid solution and prevents the slag from transforming the 2CaO·SiO₂ to type γ. It can be also said that it is necessary that the stabilizer is diffused into particles of 2CaO·SiO₂ of sizes up to 20 to 40 μm.

5 Method of Addition

Although homogeneous diffusion of the stabilizer into the molten slag can be attained with agitation methods such as bubbling or mechanical stirring by an impeller, new adoption of such agitation methods requires installation of exclusive-use facilities in the furnace vicinity; this is by no means easy where plant space is currently congested. As a method which requires no new exclusive-use facilities, the stabilizer, with its crystal water controlled to make possible homogeneous diffusion, was simply put into the slag pot prior to skimming.

The stabilizer in this study mainly consisted of borate. Particle size distribution is shown in Fig. 4. Excessively small sizes are not desirable because they invite scattering. Borate is added, as shown in Fig. 5, by placing the stabilizer (0.5 wt% of slag) in the slag pot before molten slag is skimmed.

6 Results and Discussion

6.1 Stabilization

Site photos of slag which has been stabilized by addition of the stabilizer are shown in Photo 2 (solidified slag in slag pot) and Photo 3 (stabilized slag at slag cooling yard). Identification of mineral composition is shown in
evaporation in slag with temperatures of more than 1000°C thereby generates a tremendous amount of vapour pressure. Therefore, it is necessary to adjust the energy to an appropriate level so that the stabilizer will diffuse most satisfactorily. Crystal water contents and the effect of crystal water in the stabilizer are shown in Fig. 7. The level of crystal water content in the stabilizer which gives the best stabilizing effect with K-BOP slag with the minimum addition of borate was 7%. As shown in the figure, an insufficient quantity of crystal water causes insufficient diffusion, thus requiring a larger addition of B₂O₃, and an excessive quantity of crystal water causes bubbles in the molten solution to concentrate and blow out.

6.3 Physical and Chemical Properties of Stabilized Slag

6.3.1 Abrasion test

Solidification gives slag an abrasion resistance equivalent to native stone. Its hardness was measured by an abrasion test applied to aggregate for road construction. As a result, it was found that the solidified slag had a hardness of 13 to 31% and a mean hardness of 19.3%. This means that the solidified slag is slightly harder than BF slag or limestone (about 30%) and equivalent to granite and basalt (about 20%).

6.3.2 Influences of free CaO and MgO

Since slag contains free CaO and MgO, aging occurs after slag stabilization due to hydration reactions involving these free compounds. Stabilized slag with a fineness modulus adjusted to 8 was investigated through a period of 24 weeks as shown in Fig. 8. Many samples showed practically no change, while some showed
changes down to a fineness modulus of 7.6 within the first 12 weeks. This lower fineness modulus was found in slag which contained significant amounts of free CaO or MgO. In any case, after being left standing in open air for three months, the samples showed no further changes. Thus it was found that slag aged for three months can be used as road construction material.

6.3.3 Unconfined compression strength

No hydration reaction occurs with γ-type 2CaO·SiO₂, a slow hydration reaction develops with the β type. Results of the unconfined compression strength test on stabilized slag as road construction material are shown in Table 2. Mean strength after a hydration period of 14 days was 12 kg/cm², comparable to that of HMS material (hydraulic and mechanized stabilized slag) of BF slag. In the test, samples were aged for 24 weeks and measured after sizer to HMS-25. As mentioned above, the γ type has no hydraulic property and totally fails to solidify, but when changed to β type by addition of a stabilizer, the slag shows hydraulic property and gains sufficient bounding.

Table 2 Unconfined compression strength of core sample cured for 14 days

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compressive strength (kg/cm²)</th>
<th>Average (kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.1 12.7 8.2</td>
<td>11.0</td>
</tr>
<tr>
<td>2</td>
<td>12.1 12.5 14.8</td>
<td>13.0</td>
</tr>
<tr>
<td>3</td>
<td>15.0 13.4 11.0</td>
<td>12.8</td>
</tr>
<tr>
<td>4</td>
<td>10.2 12.0 11.2</td>
<td>11.1</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td>12.0</td>
</tr>
</tbody>
</table>

6.3.4 Elution test

Results of an elution test of three typical samples are shown in Table 3. With stabilized slag like the current dusting slag, no harmful substances were detected. F content was below the effluent standard, although a certain amount of elution was observed.

7 Conclusions

As mentioned above, lumpy stainless steel slag has been obtained by the transformation of 2CaO·SiO₂ in the slag to type β, expanding the application scope of such slags. In addition, dust at the slag cooling yard has been suppressed, an improvement of its environmental conditions.

Features of the present method are summarized as follows:

(1) Since the present method is aimed at stabilizing the crystal into type β, instead of adjusting the composition of the slag, the amount of stabilizer for dusting prevention can be minimized (about 0.5 wt%), rendering the addition operation easier, while avoiding increases in slag generation.

(2) The fineness modulus of stabilized lumpy slag changes slightly upon aging. Thus the stabilized slag requires about three months' aging period before it is usable for aggregate.

(3) Stabilized slag is of the β type 2CaO·SiO₂ and undergoes a hydration reaction. The hydraulic property is preferable when slag is to be used as aggregate for road construction.

References

2. B. Yoshiki: Kobutsu-Kogaku, (1960), 491 [Gihodo]

No. 15 October 1986