KAWASAKI STEEL TECHNICAL REPORT

No.15（October 1986）

Development of Dusting Prevention Stabilizer for Stainless Steel Slag

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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 0.5% 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.

Development of Dusting Prevention Stabilizer for Stainless Steel Slag*

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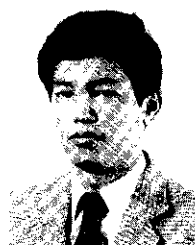Kawatetsu Mining
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1 Introduction

Stainless steel slag disintegrates into a powdery state during cooling due to transformation of $2CaO \cdot SiO_2$, thereby not only causing environmental deterioation 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.
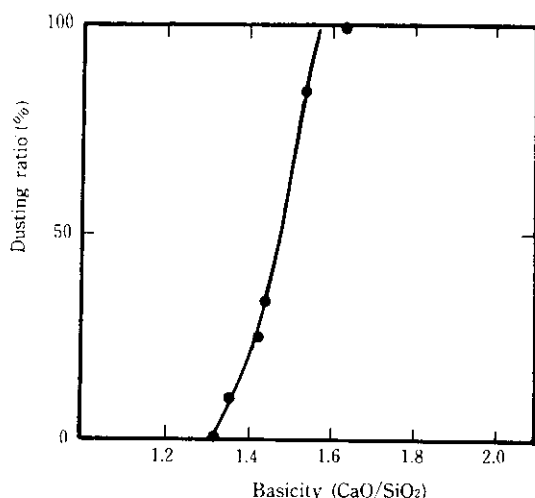
Conceivable methods for preventing this disintegration or dusting of slag include adding SiO_2 to the slag to produce $CaO \cdot SiO_2$ and adding an additive to prevent crystal transformation of $2CaO \cdot SiO_2$. The former

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 γ-$2CaO \cdot SiO_2$. 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 $2CaO \cdot SiO_2$ quantity seems to increase.

Phases of $2CaO \cdot SiO_2$ are known to be types α, α', β, and γ,[1] and the relation between transformation sequence and transformation temperature is as shown below.

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

$$\text{Liquid phase} \xrightarrow{\text{2 130°C}} \text{type } \alpha \xrightarrow{\text{1 450°C}} \text{type } \alpha' \xrightarrow{\text{850°C}} \text{type } \gamma$$
$$\left\lfloor \xrightarrow{\text{675°C}} \text{type } \beta \right.$$

Ordinarily, transformation occurs in the sequence of "type $\alpha \to$ type $\alpha' \to$ type γ," but it is known that under certain conditions transformation progresses in the sequence of "type $\alpha' \to$ type β." Density values for the respective types are

3.07 for type α
3.31 for type α'
3.28 for type β
2.97 for type γ.

Transformation from type α to type α' poses no problems from the viewpoint of disintegration, because the transformation occurs in the molten slag, but transformation from type α' to type γ is accompanied by volumetric expansion as great as about 14%,[2, 3] thereby causing dusting and complete disintegration of the slag.

3 Prevention of Dusting

The transformation from type α' to type β has almost no volumetric expansion, so dusting can be prevented simply by promoting the transformation of type α' to type β. In connection with transformation from type α' to type β, 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+}.[4]

(2) Substitution of ions having C/R (valence/ionic radius) ratio smaller than 2 or greater than 9.5.[5]

Ionic radius of B^{3+}, P^{5+} and Si^{4+} in 4-coordinations:

B^{3+} P^{5+} Si^{4+}
0.22 < 0.33 < 0.4 (Å)

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

Ba^{2+} Sr^{2+} Ca^{2+}
1.36 > 1.16 > 0.99 (Å)

(3) Addition of 5% Fe_2O_3 to form type β. However, iron oxide may change its valence number under various conditions, and one theory maintains that FeO promotes the occurrence of type γ.[7]

(4) Additions of Al and Mo to wrap $2CaO \cdot SiO_2$ with aluminate or molybdate to form type β.[8]

(5) Reduction in crystalline particle sizes by rapid cooling from high temperature without using additives to form type β.[9]

Of these methods, method (1), in which an ion of smaller ionic radius, such as B^{3+} and P^{5+}, is substituted for the Si^{4+} ion, is effective and reliable. Thus B^{3+} and P^{5+} are known as stabilizers preserving type β. A comparison of the slag stabilizing effects of borate and phosphate was made on a laboratory scale. As shown in **Fig. 2**, borate stabilizes slag at an addition level less than 1/4 that of phosphate, and is also lower in unit cost than phosphate. Therefore, borate was selected as a stabilizer.

Chemical compositions of stainless steel slag and BOF slag are shown in **Table 1**. Although there is a slight difference in composition, both contain $2CaO \cdot SiO_2$; BOF slag, however, causes no dusting. This is considered attributable to the role of P_2O_5 as a stabilizer of type β in the BOF.

Another conceivable method of preventing slag dusting is to cause the slag to assume the composition $CaO \cdot SiO_2$ instead of $2CaO \cdot SiO_2$; for this purpose, it is necessary to add about 20% SiO_2. However, it is ex-
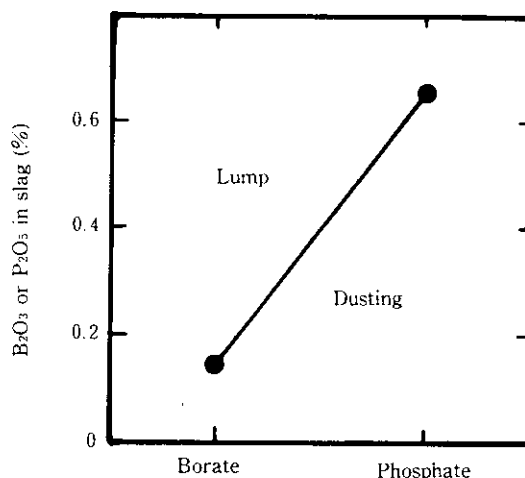

Fig. 2 Comparison of borate with phosphate for stabilization of slag.

Table 1 Chemical composition of B.O.F. and K-BOP slag

	Component (%)					Mineral composition
	CaO	SiO$_2$	P$_2$O$_5$	MgO	T. Fe	
BOF slag	40-50	10-15	2-5	2-9	15-20	2CaO·SiO$_2$, 2CaO·Fe$_2$O$_3$, MgO
K-BOP slag	48-54	32-33	0.02	10-11	0.7-0.9	2CaO·SiO$_2$, MgO

tremely difficult to add material of this composition to molten slag and achieve its homogeneous dissolution.

4 Role of Stabilizer in Slag

The action of the stabilizer on 2CaO · SiO$_2$ 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 performes 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-SiO$_2$-P$_2$O$_5$

Phase 2: CaO-SiO$_2$-P$_2$O$_5$-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 · SiO$_2$ is equivalent to Phase 1; its particle size is 20 to 40 μm.
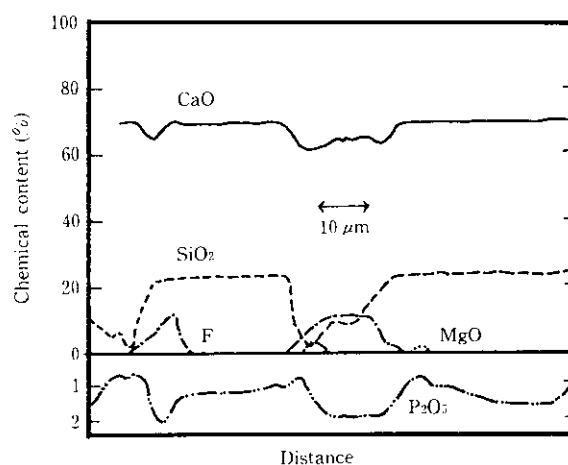(2) At the 2CaO · SiO$_2$ particle boundary, F, which seems to be fluorapatite, exists, indicating Phase 2
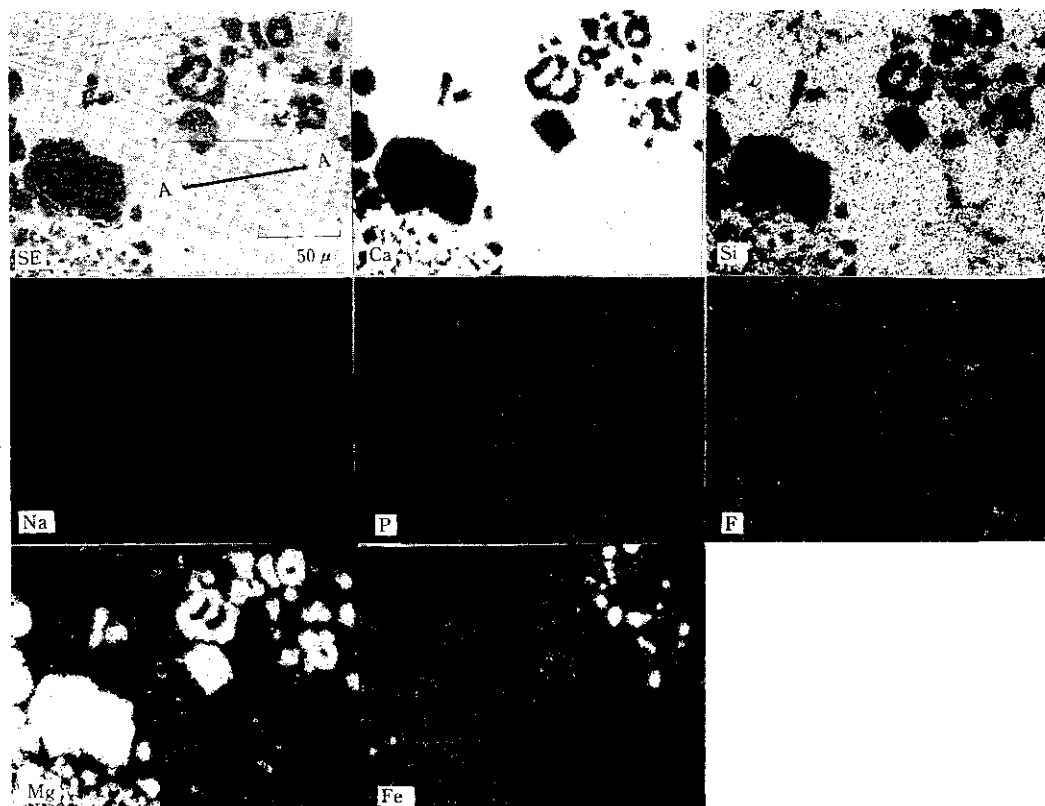

Fig. 3 Analysis of A-A' line in Photo 1

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

mineral composition.

(3) P exists in 2CaO · SiO$_2$ as solid-solution of 1 to 1.5% P$_2$O$_5$, and excess P$_2$O$_5$ is pushed to the particle boundary.

From the distribution map of P$_2$O$_5$, it is inferred that B$_2$O$_3$ is also contained in 2CaO · SiO$_2$ as solid solution and prevents the slag from transforming the 2CaO · SiO$_2$ to type γ. It can be also said that it is necessary that the stabilizer is diffused into particles of 2CaO · SiO$_2$ 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 imp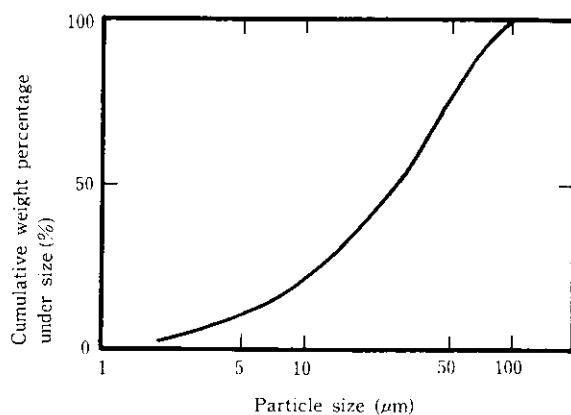eller, new adoption of such agitat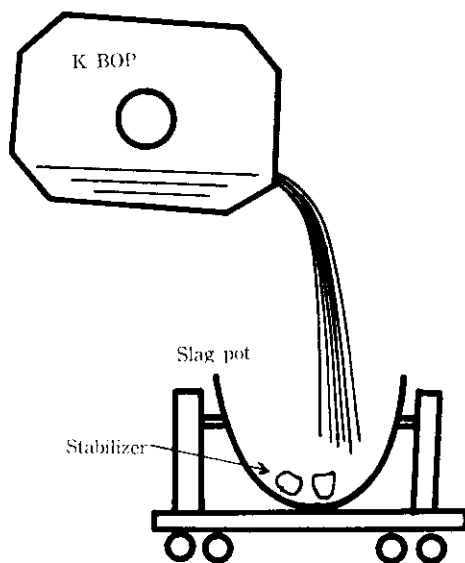ion methods requires installation of exclusive-use facilities in the furnace vicinity; this is by no means easy where plant space is currently congested. As a method which requires no new exclusive-use facilities, the stabilizer, with its crystal water controlled to make possible homogeneous diffusion, 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

Fig. 4   Particle size distribution of stabilizer

Photo 2   Stabilized slag in pot

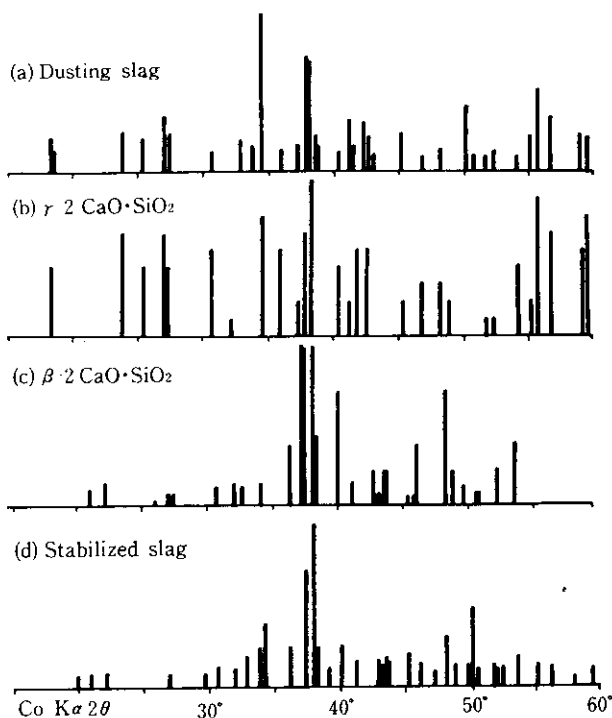Fig. 5   Method of addition

Photo 3   Stabilized slag in cooling yard

Fig. 6 X-ray diffraction pattern of dusting and stabi-
lized slag

Fig. 6. Figure 6 (a) shows dusting slag; (b) shows γ-
$2CaO \cdot SiO_2$ given in the literature, and indicates that
dusting slag belongs to type γ. Figure 6 (c) shows β-
$2CaO \cdot SiO_2$ given in the literature; and (d) shows slag
stabilized by the stabilizer. From the above, it can be said
that the stabilized slag generally belongs to type β.

6.2 Diffusion of Stabilizer

Since crystal water in the stabilizer is dehydrated and
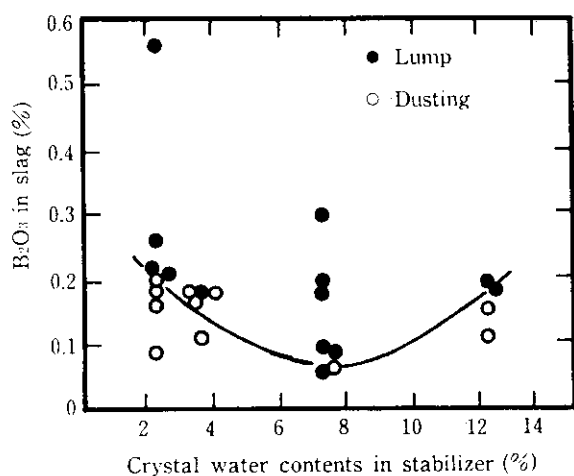evaporated at about 550°C, an instant dehydration and

Fig. 7 Effect of crystal water in stabilizer

evaporation in slag with temperatures of more than
1 000°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 B_2O_3, and an excessive quantity of crystal
water causes bubbles in the molten solution to con-
centrate 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 construc-
tion. 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
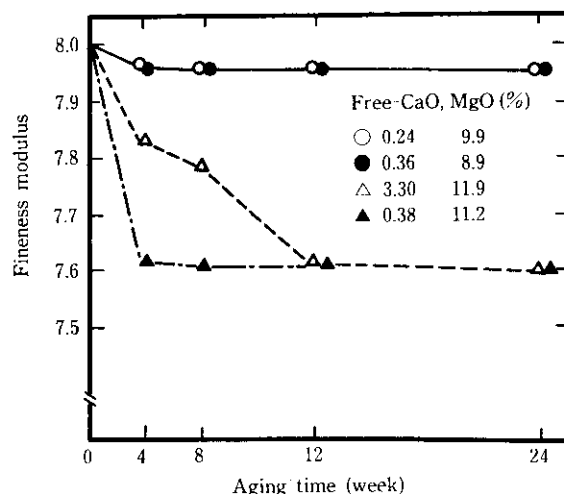showed practically no change, while some showed

Fig. 8 Relation between fineness modulus and aging
time of stabilized slag

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 $2CaO \cdot SiO_2$, 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 mechanically stabilized slag) of BF slag. In the test, samples were aged for 24 weeks and measured after sizing 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

Sample	Compresive strength (kg/cm²)			Average (kg/cm²)
1	12.1	12.7	8.2	11.0
2	12.1	12.5	14.8	13.0
3	15.0	12.4	11.0	12.8
4	10.2	12.0	11.2	11.1
$\bar{X}$				12.0

Table 3　Elution test

Sample	Cr⁶⁺	T. Cr	As	CN	F
1	ND	ND	ND	ND	5.54 (ppm)
2	ND	ND	ND	ND	9.84
3	ND	ND	ND	ND	3.23
*	<0.05	<0.5	<0.05	ND	<10

*: Effluent standards
ND: None detection

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 $2CaO \cdot SiO_2$ 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 a three months' aging period before it is usable for aggregate.
(3) Stabilized slag is of the β type $2CaO \cdot SiO_2$ and undergoes a hydration reaction. The hydraulic property is preferable when slag is to be used as aggregate for road construction.

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