Effects of Alkalis and Zinc on the Wear of Blast Furnace Refractories and the Tuyere Displacement*

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Synopsis

The Amagasaki No. 1 Blast Furnace, Kobe Steel, Ltd., was blown out in the course of operation and dissected. Complete pictures for the profiles of worn linings in different zones, particularly in the tuyere zone, were obtained and mineralogical examinations of the refractories were made with particular attention to the behaviors of alkalis and zinc. Penetration of alkalis into the brick and formation of alkali aluminosilicate which would accompany the cracking and swelling are main causes of the wear of the refractories. The turning-up of the tip of tuyere would be due to the swelling of the tuyere fireclay brick.

I. Introduction

With the recent tendency of the enlargement of a blast furnace capacity and severeness of operation, such as a higher blast temperature and higher top pressure operation, the significant wear was found at the lining of the region from the lower part of shaft to bosh and at the bottom of the hearth.1,2) Accordingly, in order to prolong the life of a blast furnace, it is necessary to make clear the wear mechanism of these refractories and to reflect the results to the proper design and construction of the furnace.

In this study, detailed observations and mineralogical examinations were carried out on the refractories of the blown-out small blast furnace. Particular emphasis was laid on the behaviors of alkalis and zinc and on the wear mechanism of the refractories at the tuyere zone.

II. Operation Data and Refractories of the Blast Furnace

In November 1976, the Amagasaki No. 1 Blast Furnace (volume: 721 m³, hearth diameter: 6.7 m) was blown out during the normal charging after 102 months’ operation and cooled down by watering to investigate the behavior of burden3) in the furnace and to obtain the profile of the worn lining. The operation data through the campaign are shown in Table 1. Total iron production amounted to 2 495-000 t, of which about 90% was foundry pig iron.

Arrangement of lining construction in the furnace and typical qualities of refractories used are shown in Fig. 1 and Table 2, respectively. The bottom of the hearth consists of two layers of carbon block (each layer is 600 mm in thickness) at the upper part and eleven layers of fireclay brick (one 450 mm layer, nine 115 mm layers and one 94 mm layer in thickness) at the lower part.

The cooling system was as follows; the shaft zone was cooled with the aid of cooling boxes. In the belly zone cooling box and water spraying on the external surface of iron shell of the furnace was used together. From the bosh to the hearth zone, the external spraying was adopted. In all cases sea water were used as a coolant. The bottom plate of the furnace hearth was cooled with air.

The refractories taken from the different positions which were specified in Fig. 1 were mineralogically examined by chemical analysis, optical and scanning electron microscopic observations, X-ray diffraction analysis and electron probe X-ray microanalysis.

III. Results and Discussions

1. Wear of the Furnace Lining

The profile of the worn furnace lining is shown in Fig. 1. The fireclay brick at the upper part of shaft

<p>| Table 1. Operation data of the Amagasaki No. 1 B. F. |
|---|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Item</th>
<th>Period</th>
<th>Iron production (t/d)</th>
<th>Productivity (t/d·m³)</th>
<th>Coke ratio (kg/t)</th>
<th>Oil ratio (kg/t)</th>
<th>Blast volume (Nm³/min)</th>
<th>Addition of oxygen (Nm³/min)</th>
<th>Top gas pressure (g/cm²)</th>
<th>Sinter ratio (%)</th>
<th>Pellet ratio (%)</th>
<th>Blast temperature (°C)</th>
<th>Slag volume (kg/t)</th>
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<tbody>
<tr>
<td>1968</td>
<td>1 074</td>
<td>1.49</td>
<td>536</td>
<td>28.2</td>
<td>1 171</td>
<td>0</td>
<td>34.9</td>
<td>75.5</td>
<td>0</td>
<td>920</td>
<td>354</td>
<td></td>
</tr>
<tr>
<td>1969</td>
<td>1 187</td>
<td>1.65</td>
<td>512</td>
<td>28.0</td>
<td>1 244</td>
<td>0</td>
<td>39.2</td>
<td>78.4</td>
<td>0</td>
<td>1 010</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>1970</td>
<td>1 187</td>
<td>1.64</td>
<td>520</td>
<td>41.9</td>
<td>1 273</td>
<td>0.2</td>
<td>37.8</td>
<td>84.9</td>
<td>4.6</td>
<td>963</td>
<td>366</td>
<td></td>
</tr>
<tr>
<td>1971</td>
<td>1 076</td>
<td>1.49</td>
<td>507</td>
<td>56.8</td>
<td>1 184</td>
<td>0.1</td>
<td>36.3</td>
<td>81.5</td>
<td>5.2</td>
<td>987</td>
<td>361</td>
<td></td>
</tr>
<tr>
<td>1972</td>
<td>972</td>
<td>1.35</td>
<td>512</td>
<td>37.9</td>
<td>1 079</td>
<td>0</td>
<td>33.2</td>
<td>80.1</td>
<td>7.0</td>
<td>999</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>1973</td>
<td>1 232</td>
<td>1.71</td>
<td>489</td>
<td>53.6</td>
<td>1 216</td>
<td>0.4</td>
<td>66.8</td>
<td>64.3</td>
<td>11.8</td>
<td>980</td>
<td>319</td>
<td></td>
</tr>
<tr>
<td>1974</td>
<td>1 183</td>
<td>1.64</td>
<td>515</td>
<td>40.9</td>
<td>1 171</td>
<td>0.1</td>
<td>66.8</td>
<td>64.3</td>
<td>13.2</td>
<td>858</td>
<td>306</td>
<td></td>
</tr>
<tr>
<td>1975</td>
<td>1 149</td>
<td>1.59</td>
<td>494</td>
<td>45.1</td>
<td>1 147</td>
<td>0.8</td>
<td>41.9</td>
<td>55.5</td>
<td>20.9</td>
<td>961</td>
<td>279</td>
<td></td>
</tr>
<tr>
<td>1976</td>
<td>1 045</td>
<td>1.45</td>
<td>494</td>
<td>48.3</td>
<td>1 100</td>
<td>0</td>
<td>39.3</td>
<td>54.8</td>
<td>24.3</td>
<td>1 042</td>
<td>263</td>
<td></td>
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</tbody>
</table>

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*** Amagasaki Works, Kobe Steel, Ltd., Ohama-cho, Amagasaki 660.
hardly wore, but increase in the joint thickness of bricks and rounding of the edge of brick at the inner surface of the wall were observed. The lower the position of the furnace was, the more violent the wear of the furnace lining. From the middle part of shaft to the upper part of bosh, the lining almost dis-

![Image of worn lining profile](image1)

![Image of wear state of lining](image2)

Table 2. Original properties of the refractories used in the Amagasaki No. 1 B.F.

<table>
<thead>
<tr>
<th>Refractories</th>
<th>Fireclay brick</th>
<th>Carbon block</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S-10</td>
<td>S-20</td>
</tr>
<tr>
<td>Position</td>
<td>Upper part</td>
<td>Middle part</td>
</tr>
<tr>
<td></td>
<td>of shaft</td>
<td>and lower part of bottom</td>
</tr>
<tr>
<td>Refractoriness SK</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.18</td>
<td>2.20</td>
</tr>
<tr>
<td>True density (g/cm³)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Apparent porosity (%)</td>
<td>16.5</td>
<td>14.0</td>
</tr>
<tr>
<td>True porosity (%)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Compression strength (kg/cm²)</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Refractoriness under load of 2 kg/cm², Tₐ °C</td>
<td>—</td>
<td>1445</td>
</tr>
<tr>
<td>Chemical composition (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>56.5</td>
<td>55.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>37.0</td>
<td>41.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.68</td>
<td>1.60</td>
</tr>
</tbody>
</table>

* V. M.: Volatile matter  
** F. C.: Fixed carbon

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remarkably that the upper two layers among the five layers of carbon block completely disappeared, and the block of the lowest layer became less than half in radial thickness of the original lining and had numerous cracks all over the block. Fireclay brick installed between the tuyeres was also worn significantly at the upper part and cracked with numerous laminations in parallel with the surface of the brick. Further, this cracked brick swelled in 105~130% of the thickness of the original brick and turned up the inner side of the brick. This swelling causes the displacement of the lowest layer of bosh carbon block upwards by about 50 mm and, therefore, the formation of the wedge-shaped peripheral gap at the joint of the carbon block and fireclay brick layers in the vicinity of the iron shell of the furnace.

On the brick around the tuyere, the profile of the worn lining and the turning-up phenomenon of the brick are similar to those of fireclay brick installed between the tuyeres as shown in Fig. 3. The axis of tuyere had been forced to be inclined by about 2° against horizontal, which was measured by clinometer. Carbon block beneath the tuyere fireclay brick was disintegrated in about 120 mm in thickness near the boundary with fireclay brick and the material which mainly consisted of the blast furnace slag was found to penetrate to the disintegrated part.

Carbon block of the hearth zone almost remained in the original state together with the protecting brick, except for the refractories just above taphole and under slaghole. Carbon block above taphole was remarkably worn with some large cracks in which powder of crumbled carbon block existed. In the bottom zone of the hearth, all of the carbon blocks and the upper two layers of fireclay brick disappeared. From tuyere to hearth, scab formed on the lining, of which thickness was 300~400 mm in the tuyere zone and 200~300 mm in the hearth. Such a scab continued to the salamander on the bottom of the hearth. A titanium bear was scarcely observed in the furnace. This may be the result of such an operation that foundry pig iron was mainly produced and therefore the amount of TiO2 in burden was limited to the low level of 2~3 kg/t-pig.

2. Penetration of Foreign Elements and Wear of Refractories

In the neighboring part of the surface of fireclay brick, various foreign elements penetrated into the brick as shown in Fig. 4. A great deal of potassium was involved in the brick in the region from the middle part of shaft to tuyere, where the lining was very heavily worn. From the results of chemical analysis on the fireclay brick in this region, the potassium content was high near the surface of brick as shown in Figs. 5 and 6. According to the results of the X-ray diffraction, potassium in the brick was found to be kalsilite (K2O·Al2O3·2SiO2). On the other hand, the penetration of sodium was about 3% at the most and less than one fifth of that of potassium. Zinc had a tendency to penetrate into the inward of the brick and it was determined as zincite (ZnO) and willemite (ZnO·SiO2). Penetration of carbon corresponded to that of potassium. Thus, foreign elements in the fireclay brick were proved to be mainly alkalis and carbon.

On the penetration of foreign elements into bosh carbon block, alkalis much penetrated as shown in Fig. 7. Carbon block with alkalis of about more than 3% had numerous cracks all over the block. According to Konishi et al.,4) carefully deashed coke reacted with elementary potassium vapor and was cracked by more than 4% of potassium. From these facts, the wear of carbon block can be considered to be mainly caused by the alkali penetration. On the other hand, zinc content in the block was very low. This was mainly due to the low input of zinc 0.2~0.3 kg/t-pig into the furnace and the condition of relatively high temperature inside the block, which was estimated from the coke temperature of more than

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![Fig. 3. Wear state of the fireclay brick around No. 8 tuyere and turning-up of the tuyere tip.](image)

![Fig. 4. Foreign elements in the vicinity of the surface of fireclay brick and distribution of alkalis in burdens.](image)
As mentioned above, the alkali penetration into the furnace lining is so significant that it causes the wear of refractories. This phenomenon is closely related to the behavior of alkalis in the blast furnace. For example, the distribution of alkalis in burden inside the furnace considerably corresponds to that in the lining as shown in Fig. 4. Further, as it is well-known, alkalis may circulate in the high temperature region of the furnace as shown in Fig. This may mean that alkali silicates in burden are reduced to elementary alkali and alkali cyanide vapors in the high temperature region of the furnace. Accordingly, the refractories in the region from the lower part of shaft to the bosh zone are apt to be attacked by these vapors.

The wear of fireclay brick is mainly due to the formation of kalsilite in accordance with the reaction given by Eq. (1) and its volume expansion (calculated volume change is about 6%8)).

\[ 6K^+ + 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2 + 3\text{CO} = 3(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 3\text{C} \]...........(1)

Hayashi and Shibuno\textsuperscript{9)} explained that alkali vapor forms liquid phase by the reaction with glass and cristobalite in the brick besides the formation of alkali aluminosilicates, and this may lead the deterioration of brick and may accelerate the wear. As shown in Fig. 6, when alkalis content in fireclay brick was over 15% as K\textsubscript{2}O, such a brick cracked in parallel with the surface and swelled. Many stratified cracks were observed in the broken part of brick than near the surface. One of the reasons may be crystallization of the rodlike kalsilite and carbon deposition proceeded significantly near the surface, because of long time exposure to high temperature. Based upon Eq. (1) carbon deposits at the same time with the formation of kalsilite.
of kalsilite. This is confirmed from the relationship between the K₂O and carbon contents in fireclay brick of shaft and tuyere zones as shown in Fig. 9.

In the disintegrated tuyere brick near the surface, the carbon content was much higher than that calculated from Eq. (1). In this case it was considered that the carbon deposition reaction represented by Eq. (2) and/or the reaction with alkali cyanide vapors occurred at the same time with the reaction given by Eq. (1).

\[
2\text{CO} = \text{CO}_2 + \text{C} \quad \text{(2)}
\]

It is also supported from the fact that swelling of the brick near the surface was more than the volume expansion of about 6% expected from reaction (1), as shown in Fig. 2. Thus, concerning swelling of fireclay brick, the other mechanisms such as carbon deposition reaction have to be considered besides alkali penetration.

Swelling and cracking of carbon block were also related to the penetration of alkalis as mentioned above.

3. Formation of Alkali Aluminosilicate

It was confirmed that, when the average content of K₂O in fireclay brick was more than about 15%, alkali aluminosilicate such as kalsilite was detected. To clarify the formation mechanism of kalsilite and its behavior in brick, the specimens which were taken from the brick installed between tuyeres were fractured compulsively and morphologically examined.

Scanning electron micrographs (SEM) of the fracture surface and optical micrographs (OM) of the specimen were shown in Photo. 1. Microstructure of the fractured surface obviously changed with the increase in average content of K₂O in the brick. The surface of specimen ① with the K₂O content of 0.3% looked like that of the original brick. In the specimen ② with the K₂O content of about 5%, however, precipitation of potassium or potassium compounds was observed on the internal surface of the brick and in the specimen ③ with the K₂O content of about 18%, many rodlike crystals and the globular crystals with microcrack as seen in the middle part of the SEM appeared. Moreover, in the specimen ④ with the K₂O content of about 20%, the globular crystals and the original structure of the brick disappeared and only rodlike crystals which accompanied fine particles were observed. Thus, the formation of loose structure by the growth of the rodlike crystal must deteriorate the strength of the brick.

According to the results of EPMA and X-ray diffraction, in the specimens ① and ②, potassium, zinc and carbon concentrated near the pore of brick, but the structure was not changed. In the specimen with more than 15%K₂O, the structure was composed of kalsilite and graphite, which were recognized as angular rodlike crystal and fine particle, respectively.

Based upon the results, the formation of alkali aluminosilicate would be explained as follows; potassium, zinc and carbon monoxide penetrate into fireclay brick as the gaseous phase through the pore and crack, and they deposit or react with the brick. When potassium vapor and carbon monoxide react with mullite and α-cristobalite in fireclay brick, glassy and crystalline alkali aluminosilicates are formed. The silicate accompanying the deposited carbon grows into rodlike kalsilite crystal. Therefore actual swelling of fireclay brick by the alkali penetration is larger than that by the change of the mineral phase based upon Eq. (1). Some of the authors have already reported that the hardness of the fireclay brick into which potassium penetrated over 15% as K₂O, remarkably decreased as shown in Fig. 10.

Consequently it has been considered that the alkali penetration deteriorated fireclay brick in its microstructure with cracking and swelling, and at last crumbled it as so-called alkali bursting.

4. Tuyere Displacement

As mentioned above, fireclay brick shows remarkable swelling by the formation of alkali aluminosilicates.

If the furnace lining above the tuyere, particularly bosh lining, disappears, the tuyere brick is less sustained. This situation made it easy to turn up the
inner side of the brick by the swelling as shown in Fig. 2. It would be suggested that such a displacement of the tuyere brick makes the tip of the tuyere move the same direction. The movement of the tuyere shown in Fig. 3 would be mainly caused by alkali attack to the tuyere brick. From such a point of view, in order to prevent the tuyere displacement which has often led to the tuyere burnout, it is necessary to use the brick of low porosity and high resistance for alkali attack to the tuyere brick. In addition, it is one of the important techniques to design the brickwork so as to reduce the number of the joint of bricks by the use of large size bricks. In order to conduct an effective cooling of the tuyere zone in the blast furnace, it is required to consider the tuyere cooling design and the cooling experience in the actual blast furnaces.
order to suppress the alkali reaction.

**IV. Conclusion**

Observation and mineralogical examination on the lining refractories of the blown-out Amagasaki No. 1 Blast Furnace, Kobe Steel Ltd., were carried out. Particular emphasis was laid on alkalis and zinc penetrations into the refractories and their effects on the wear of refractories.

The main cause of the wear of refractories at the furnace wall was found to be alkali attack due to penetration of alkali vapor. Formation and growth of alkali aluminosilicate such as kalsilite in fireclay brick, accompanying the cracking and remarkable swelling, brought about the turning-up of the tip of a tuyere, which has often led to the tuyere burnout. Accordingly development of refractories having superior resistance for alkali attack, improvement of designing and constructing the brickwork and such an operation to remove the alkalis from the furnace should be pursued for the longer life of the blast furnace.

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