FREEZING AND THAWING RESISTANCE OF STEEL-MAKING SLAG CONCRETE

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Steel-making slag concrete consisted of by-products from ironworks. Ground granulated blast furnace slag was used as a binder. Air cooled slag from the steel-making process was used as an aggregate. The steel-making slag concrete did not use any natural aggregate, fine or coarse. The strength of the steel-making slag concrete was 20 N/mm² to 50 N/mm² at 28 days. It was as strong as that of normal cement concrete. Resistance to carbonation of the steel-making slag concrete and resistance to corrosion of a steel rod in the steel-making slag concrete were high for a long time due to calcium hydroxide leaching from the steel-making slag. However, resistance to freezing and thawing of the steel-making slag concrete was low. In this paper, the mechanism of low resistance to freezing and thawing is clarified.

Key Words: steel-making slag concrete, resistance to freezing and thawing, calcium hydroxide, air distribution, AE agent, pozzolan

1. INTRODUCTION

Blast furnace slag is a by-product from a blast furnace producing pig iron from iron ore. Slag produced is about 290kg per ton of pig iron. On the other hand, steel-making slag is produced in the process of making steel from pig iron. Such slag produced is about 110kg per of one ton of steel. In 2004 Japan produced blast furnace slag and steel-making slag of 25 million tons and 14 million tons, respectively1). Ground granulated blast furnace slag is used as a binder in concrete. Steel-making slag has been used as a soil improvement material or a roadbed material. In Japan, it is not used as aggregates in concrete. The aggregate used in this project of steel-making slag concrete was steel-making slag. Steel-making slag concrete is expected as a material reducing environment load2). After many demonstrations of construction with steel-making slag concrete were carried out, a technical manual for steel-making slag concrete was published3).

The strength of steel-making slag concrete varied from 20 N/mm² to 50 N/mm². Calcium hydroxide leaching from the steel-making slag stimulates a ground granulated blast furnace slag. Cement is not required in order to harden steel-making slag concrete. It is known that resistance to sulfate attack of steel-making slag concrete is superior to that of normal cement concrete4). But, resistance to freezing and thawing of steel-making slag concrete is inferior to that of non-AE concrete. Therefore, geographical area where steel-making slag can be used is restricted to warm weather. The improvement of resistance to freezing and thawing of steel-making slag concrete is necessary to enlarge the area where steel-making slag concrete can be used. The mechanism and improvement method to freezing and thawing are shown in this paper.
2. OUTLINE OF THE EXPERIMENT

(1) Materials and mixture proportion

Ground granulated blast furnace slag and fly ash were used as a binder. The density of ground granulated blast furnace slag was 2.89 g/cm³ and the specific surface area by Blain was 4,000 cm²/g. The density of fly ash was 2.20 g/cm³. Lime dust and ordinary portland cement were used as alkali activators. The density of lime dust was 3.14 g/cm³, and that of ordinary portland cement was 3.15 g/cm³. Steel-making slag sand (density: 3.06 g/cm³, water absorption: 7.67%), blast furnace slag sand (density: 2.71 g/cm³, water absorption: 1.28%), and river sand (density: 2.58 g/cm³, water absorption: 1.95%) were used for fine aggregate. Steel-making slag gravel (density: 3.18 g/cm³, water absorption: 4.50%) and crushed stone (density: 2.74 g/cm³, water absorption: 0.59%) were used for coarse aggregate. Furthermore, the weak surface of the steel-making slag was scoured off by Los Angeles machine in order to improve the quality of the slag. Steel-making slag aggregate with different types of surface characteristic and water absorption was made by changing the number of rotations of Los Angeles machine as shown in Fig. 1. Table 1 shows Property of aggregate used in this study.

Mixture proportion of standard steel-making slag concrete is shown in Table 2. Table 1 shows mixture proportions of steel-making slag concrete used in this study. Amount of water, amount of coarse aggregate, volume of binder, and sand-total aggregate ratio were held constant for different mixture, Table 3.

Polycarbonate high-range water reducing agent and Air-entraining agent were used for admixture. Table 2 shows mixture proportion of standard steel-making slag concrete.

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(2) Property of steel-making slag

Table 4 shows chemical composition of the steel-making slag. Steel-making slag contained metallic elements such as iron or manganese. Therefore, the density of the steel-making slag was high. Quantity of calcium oxide content was also high. Unless the steel-making slag is did aging adequately, in other word free-Ca and free-Mg in steel making slag is changed to a stable material, it expands in the steel-making slag concrete and eventually breaks the concrete in pieces. By the way, steel-making slag includes a lot of iron, but the surface of the steel-making slag concrete is pure in the same way as normal cement concrete.

Fig. 2 shows the change of pH of water with the steel-making slag. Measuring pH of steel-making slag used solution that soaked and stirred the 50g steel-making slag 10 times by mass with distilled water. The circles represent the results of non-washed steel-making slag. The squares represent the results of washed steel-making slag. pH of the water with washed steel-making slag increased with time. Therefore, it was concluded that the steel-making slag leached a lot of calcium hydroxide or calcium oxide.

Fig. 3 shows the resistance to freezing and thawing of the steel-making slag, crushed stone, and recycled aggregate. The size of aggregate used for freezing and thawing test was from 15 mm to 20 mm. The samples were cyclically exposed to -18 °C to 5 °C, every 5 hours in water. Resistance to freezing and thawing of aggregate was judged by the ratio of crushed aggregate to the initial aggregate. It is clear that the resistance to freezing and thawing of the steel-making slag was the better than that of recycled aggregate and that it was almost same as that of crushed stone.

(3) Method of test

100 by 100 by 400 mm prism specimen was used for freezing and thawing test. It was cured in water for two weeks after 4 hours of steam curing at 65 °C. The specimens were cyclically exposed to -18 °C and 5 °C, every 5 hours in water. Resistance to freezing and thawing was judged by relative dynamic Young’s modulus. Air content of the fresh concrete

Table 4 Chemical composition of steel slag

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Total-Fe</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>S</th>
<th>P₂O₅</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blast furnace slag</td>
<td>41.7</td>
<td>33.8</td>
<td>0.4</td>
<td>7.4</td>
<td>13.4</td>
<td>0.80</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Steel-making slag</td>
<td>45.8</td>
<td>11.0</td>
<td>17.4</td>
<td>6.5</td>
<td>1.9</td>
<td>0.06</td>
<td>1.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Andesite (ex.)</td>
<td>5.8</td>
<td>59.6</td>
<td>3.1</td>
<td>2.8</td>
<td>17.3</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>

5 °C, every 5 hours in water. Resistance to freezing and thawing of aggregate was judged by the ratio of crushed aggregate to the initial aggregate. It is clear that the resistance to freezing and thawing of the steel-making slag was the better than that of recycled aggregate and that it was almost same as that of crushed stone.
was measured by the pressure method. Air distribution of the hardened concrete was observed by microscope. The specimen was irradiated by ultraviolet rays after it was soaked by fluorescent paint.

3. DISCUSSIONS OF TEST RESULTS

(1) Influence of water absorption of steel-making slag

Fig. 4 shows the resistance to freezing and thawing of the steel-making slag concrete whose mixture proportion is shown in Table 1. Specimen is judged to have failed when relative dynamic Young’s modulus falls below 60%. The concrete which has not failed until 300 cycles is judged to be durable. In one method, specimens were frozen and thawed out in water. In the other method, specimens were frozen in air and thawed out in water. The test results by two methods are shown in Fig. 4. Normally, the specimen failed faster when it was frozen and thawed out in water than when specimen was frozen in air and thawed out in water. Steel-making slag concrete was failed within 15 cycles by either method. Photograph 1 shows the failed specimen, which attacked by freezing and thawing action. Steel-making slag concrete failed at very early stage of the test.

Fig. 5 shows the relationship between compressive strength at 28 days and total water absorbed in the steel-making slag aggregate $\Delta \omega$. Total water content in steel-making slag aggregate $\Delta \omega$ was calculated by Equation (1). The steel-making slag, whose weak part was scoured off by the Los Angeles machine, was used in order to obtain the result shown in this figure.

\[
\Delta \omega = \frac{S \cdot Q_S}{100 + Q_S} + \frac{G \cdot Q_G}{100 + Q_G} \quad (1)
\]

Here, $S$ is unit content of fine aggregate ($\text{kg/m}^3$), $Q_S$ is water absorption of fine aggregate ($\%$), $G$ is unit content of coarse aggregate ($\text{kg/m}^3$), $Q_G$ is water absorption of coarse aggregate ($\%$). It is clear that the strength of concrete with low water absorption sand is high. Fig. 6 shows the result of resistance to freezing and thawing of the steel-making slag concrete when the water absorption of the steel-making slag sand is 7.67%. The circles, triangles, and boxes represent the result of the steel-making slag concrete with the steel-making slag gravel whose water absorption is 4.50%, 3.19% and 2.02%. Fig. 7 shows the result of resistance to freezing and thawing of steel-making slag concrete when the water absorption of steel-making slag gravel is 4.50%. The circles, triangles and boxes represent the result of the steel-making slag concrete with the steel-making slag sand whose water absorption is 7.67%, 5.96% and 3.77%. When water absorption of the steel-making slag sand is high, the influence of water absorption of gravel on resistance to freezing and thawing of the steel-making slag concrete is small. However, even if water absorption
of the steel-making slag gravel is high, the difference of the results in water absorption of the steel-making slag sand is clear. That is, the effect of water absorption of fine aggregate on resistance to the steel-making slag concrete is bigger than that of coarse aggregate.

The effect of water absorption of both sand and gravel on resistance to freezing and thawing is shown in Fig. 8. Even if both the steel-making slag sand and gravel of the smallest water absorption are used, resistance to freezing and thawing is not good. Fig. 9 shows the effect of total water content in the steel-making slag on the durability factor. As clear from this figure, the durability factor is
improved when the total water content in the aggregate $\Delta \omega$ is small. Durability factor was calculated by the following equation.

\[
\text{Durability factor} = \frac{P \times N}{300} \quad (2)
\]

Here, $P$ is the relative dynamic Young’s modulus. $N$ is the number of cycles when relative dynamic Young’s modulus reaches $P$. That is, durability factor is 100% when relative dynamic Young’s modulus is 100% at 300 cycles.

(2) Entrained air by AE agent

Fig. 10 shows the effect of air content on the resistance to freezing and thawing of the steel-making slag concrete with steel-making slag with the lowest absorption. Notation “1A” in this figure means that the standard dosage of AE agent was used. That is, 80 A means that the concrete contains 80 times as much AE agent as standard dosage was used. The resistance to freezing and thawing was improved when 80A AE agent was used, although the compressive strength became small 20% less. Fig. 11 shows the relationship between air content of the steel-making slag concrete and the dosage of AE agent. When ordinary steel-making slag was used, the air content increased with the dosage of AE agent. When the steel-making slag with low water absorption was used, the effect of AE agent was small. Fig. 12 shows the effect of the AE agent on air content of the concrete. Ground granulated blast furnace slag was used as binder without any cement. Aggregate was natural aggregate. The air content did not increase with the AE agent. Photograph 2 shows the cross section of the steel-making slag concrete. The air content of fresh concrete was over 4.5%. However, air was not well distributed in the paste. Big size air existed near the steel-making slag sand.

Fig. 13 shows the effect of cement content on the air content. Sand was river sand. Gravel was crushed stone. When natural aggregate was used, concrete without cement could not contain entrained air. On the other hand, the effect of AE agent on air content becomes big with cement content. Photograph 3 shows the cross section of the steel-making slag concrete with cement. It is clear that air is uniformly distributed in the cement paste. However, large air pocket exists near the steel-making slag sand. The air near
the steel-making slag seems to be influenced by the calcium oxide leaching from the slag.

Fig. 14 shows the result of compressive strength of steel-making slag concrete with cement. It is clear that the higher the cement content, the higher the compressive strength. Fig. 15 shows the effect of cement content on resistance to freezing and thawing of steel-making slag concrete. As the cement content increased, the resistance to freezing and thawing of steel-making slag concrete improved. But, it was still less than 200 cycles at which the specimen failed, even though the cement to binder ratio was 40%. Fig. 16 shows the relationship between the cement to binder ratio and durability factor.

Fig. 17 Effect of air content on resistance to freezing and thawing of steel-making slag concrete with cement

Fig. 18 Effect of fine aggregate type on resistance to freezing and thawing of the steel-making slag concrete. As the cement content increased, the resistance to freezing and thawing of steel-making slag concrete improved. But, it was still less than 200 cycles at which the specimen failed, even though the cement to binder ratio was 40%. Fig. 16 shows the relationship between the cement to binder ratio and durability factor.
factor. When cement was half of binder, durability factor was 25%. It did not have the minimum desirable durability factor of 60%. Fig. 17 shows the effect of air content on resistance to freezing and thawing of the steel-making slag concrete with cement. The effect of air content on the resistance to freezing and thawing of the steel-making slag concrete with cement was small when air content was over 5%.

(3) Effect of fine aggregate type

Fig. 18 shows the test result of the resistance to freezing and thawing of the steel-making slag concrete when granulated blast furnace slag sand was replaced with a part of steel-making slag sand. Little calcium hydroxide leached from the granulated blast furnace slag sand. When half of the steel-making slag sand was replaced with the granulated blast furnace slag sand, the effect of replacement was not clear. However, when all of the sand was granulated blast furnace slag sand, the steel-making slag concrete did not fail at 200 cycles. But when granulated blast furnace slag sand was used, entrapped air was over 7% as shown in Fig. 19. Therefore, a deforming agent was used in order to remove the entrapped air before the use of the AE agent. Photograph 4 shows the cross section of the steel-making slag concrete with cement and granulated blast furnace slag sand. Any large air bubbles around aggregate were not found and small size air bubbles were distributed in the paste. Fig. 20 shows the result of the compressive strength test of steel-making slag concrete with fly ash.
strength test of the steel-making slag concrete with granulated blast furnace slag sand. When more of the steel-making slag sand was replaced with the granulated blast furnace slag sand, the compressive strength of the steel-making slag concrete increased.

(4) Effect of pozzolan

Photograph 5 shows the cross section of the steel-making slag concrete with cement and granulated blast furnace slag sand. Calcium hydroxide accumulated around coarse aggregate. Calcium hydroxide around aggregate is a weak point. Fig. 21 shows the compressive strength of the steel-making slag concrete with fly ash. Cement to binder ratio was 40%. Sand was granulated blast furnace slag sand. When fly ash to binder ratio increased, compressive strength of the steel-making slag concrete decreased. However, resistance to freezing and thawing improved by fly ash as shown in Fig. 22. Cement to binder ratio of the concrete to get the results shown in this figure was 40%. Sand was granulated blast furnace slag sand. Entrapped air was removed by deforming agent before the use of the AE agent. Steel-making slag concrete did not fail at over 450 cycles when fly ash to binder ratio was 30%. But when fly ash to binder ratio was 60%, the steel-making slag concrete failed at 150 cycles.

Photograph 6 shows the cross section of the steel-making slag concrete in which fly ash was 30% of the binder. On the other hand, Photograph 7 shows the cross section of the steel-making slag concrete in which fly ash is 60% of binder. There were few air bubbles in the paste. Photograph 8 shows the cross section of the steel-making slag concrete without fly ash. Calcium hydroxide appears around gravel. On the other hand, Photograph 9 shows the cross section of the steel-making slag concrete in which fly ash was 30% of binder. Calcium hydroxide can not be observed around gravel in that mixture. Mixture proportion of an ideal steel-making slag with high resistance to freezing and thawing is shown in Table 5.

Photograph 6 Cross section of steel-making slag concrete that is most superior in resistance to freezing and thawing

Photograph 7 Cross section of steel-making slag concrete that fly ash to binder ratio is 60%

Photograph 8 Cross section of steel-making slag concrete with cement without fly ash

Photograph 9 Cross section of steel-making slag concrete with cement and fly ash
4. Conclusion

Low resistance to freezing and thawing of the steel-making slag concrete was due to small amount of entrained air by the AE agent. Air by the AE agent could not increased without cement. Furthermore, the size of air bubbles becomes large because the AE agent reacts with calcium hydroxide leaching from the slag. The use of the granulated blast furnace slag sand was effective to restrict the leaching of calcium hydroxide. Even if cement and granulated blast furnace slag sand were used, resistance to freezing and thawing of steel-making slag concrete was not satisfied. That was due to calcium hydroxide being accumulated around the gravel. Adequate quantity of fly ash is necessary to consume calcium hydroxide around the aggregate. It is important to control the calcium hydroxide in the steel-making slag concrete in order to improve the resistance to freezing and thawing of the steel-making slag.

REFERENCES


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