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Study on Utilization of Converter Slag as Concrete Admixture

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Converter has been slag produced 10 million tons per year in Japan. It is a steel making by product produced in the same way as the blast-furnace slag. Though blast-furnace slag is being used effectively as a concrete admixture, the converter slag has never been used effectively because of the expansion action of contained free lime and iron oxide. This is an important environmental problem in the steel industry. Beta-$2CaOSiO_2$ (beta-C_2S) is contained 40 percent in converter slag, therefore it is very promising as a concrete admixture. We proposed an accelerated aging processes capable of stabilizing the converter slag in a short time. The converter slag is dipped into alkali aqueous solution after heating at low temperature. It was subsequently ground to a grain size of 75 μ m , inner 30 percent of OPC. The properties of mortar and concrete using the blended cement were determined. As a result, it has become apparent that the expansion was reduced and long term compressive strength was increased while that at early ages was not so remarkable. The hydration exotherm rate was lower than that of the OPC.
Key word : converter slag, aging, beta-C_2S, free lime, concrete admixture

Introduction

Converter slag has been produced 10 million tons per year in Japan. It is a industry by product produced in the steel making process in the same way as the blast-furnace slag. The converter slag is being used as a landfill and a roadbed material in the highway and the ground stabilizing material.[1] But, it is expected to be used more effectively as a value added product.

This is a important environmental problem in the steel industry. Some research reports dealt with the use of converter slag as an aggregate for the concrete, but very few research reports on the use of converter slag as a binder material has been published.[2]

Beta - $2CaOSiO_2$ (beta - C_2S) is contained 40 percent in converter slag, therefore it is very promising as a concrete admixture.

Factors preventing the effective use of the converter slag may be attributed to an insoluble free lime left in the melt in the iron manufacture process, and the iron oxide(FeO) that remains also as an expansive agent.[3] At present, long time outdoor exposure is done as an aging process for the free lime removal. But, six months are needed, and large area is necessary for the outdoor exposure. Thus, steam aging is employed as an accelerated aging process. It is sometimes difficult even for this process to perform aging the converter slag entirely in the same way as the outdoor exposure.[4],[5],[6]

We proposed an accelerated aging processes capable of stabilizing the converter slag in a short time.

The new method is to dip the converter slag into alkali aqueous solution after heating at low temperature.

This study deals with the volume stabilization and strength, hydration exoergic property and others when a processed converter slag was used as an admixture for the concrete.

Materials and Methods

Materials

The converter slag specimen has a grain size ranging from 0.15 to 5 millimeters. The chemical composition of the converter slag is shown in table.1. Material used in the experiment is shown in table.2. The abbreviation of table.2 will be used hereafter.

Methods

Expansion stabilizing treatment (aging)

The converter slag was crushed to have a grain diameter from 0.15 to 5 millimeters, and was heated in the electric furnace at 450 degrees C. for 2 hours. Then the converter slag was dipped in the pure water or the saturated calcium hydroxide ($Ca(OH)_2$) aqueous solution for seven days. These two kinds of alkali aqueous solution were used as a stimulant of the converter slag. After the treatment, it was crushed in the ball mill to have a grain diameter less than 75 micrometers as an admixture sample.

Expansion stabilization test

The following tests were executed in this research to examine the stabilization of the expansion of the converter slag.

table.1 Chemical composition of the converter slag

Ig.loss	CaO	T-Fe	SiO2	MgO	MnO	P_2O_5	Al_2O_3	F	V	TiO_2	T-S	Na_2O	K_2O	Total
6.44	39.75	18.82	10.72	6.78	3.82	1.97	1.83	0.49	0.69	0.63	0.067	0.02	0.01	92.04

table.2 Material used in the experiment

Materials	Notation		Reference
Cement	C		Ordinary portland cement Specific Gravity 3.16g/cm^3 Blaine 3270cm^2/g
Fine aggregete	S		River sand Specific Gravity 2.62g/cm^3 Absorption 1.36% F.M. 2.52
Converter slag	CS	ST	Without treatment Specific Gravity 3.40g/cm^3 Blaine 4862cm^2/g
		B	With herting Specific Gravity 3.35g/cm^3 Blaine 4934cm^2/g
		W	With immersion in water after herting Specific Gravity 3.57g/cm^3 Blaine 4284cm^2/g
		Ca	With immersion in Ca(OH)^2 aquaous after herting Specific Gravity 3.56g/cm^3 Blaine 6510cm^2/g
Blast furnace slag	BS		Specific Gravity 2.92g/cm^3 Blaine 4640cm^2/g

Free lime measurement

Free lime content was determined by Frank method. Each the samples of a grain diameter of 0.15, 0.3, 0.6 , 1.2 and 2.5 millimeters were subjected to test before and after heating, and after 1, 3 and 7 days immersion in water and the $Ca(OH)_2$ aqueous solution.

State of ferro oxidizes on the surface of the converter slag

The state of ferro oxidizes on the surface of a particle of the converter slag with or without treatment was determined by the X-rays photoelectron spectroscopic analysis (XPS).

Identification of the principal minerals

Minerals were measured for the converter slag without treatment(ST), with heating (B) and with immersion in the water(W) by the powder X-ray diffraction(XRD).

Length change measurement

To measure the expansion due to free lime and FeO that remain in the converter slag, sealed cured mortar specimens at the age of 7 days were held in the atmospheree of the relative humidity of 100 percent at 20 degrees C., and the length change was measured. Mix proportion of mortar was based on the standard strength test of the cement (JIS R 5201-1992) , and water-binder ratio was made 55 percent. The admixture substitution was inner 70 percent of PL that was the mix of only OPC. The admixture samples were granulated blast-furnace slag(BS) as a comparative material, ST, W and Ca. Mortar specimen dimension was 4 centimeters high, 4 centimeters wide, 16 centimeters long and the determination of length change was based on the standard length change test (JIS R 1129-1993), dial gauge method , at the age of 3, 7, 14, 28, 56, 91 days.

Evolution as an admixture

The following tests were done in this research to examine the applicability of the converter slag as an admixture.

Compressive strength test

Mix proportion of the mortar specimen was based on the standard test of cement(JIS R 5201-1992), and a water-binder ratio was 55 percent. An admixture substitution rate was inner 30 percent of PL that was the mix of only OPC. The admixture samples were granulated blast-furnace slag(BS) as a comparative material, ST, W and Ca. Mortar specimen was a cylinder of 5 centimeters in diameter, 10 centimeters high, and measured in the age of 7, 28, 91 days. The mortar specimen was subjected to sealed curing until the age of 7 days, and then put in the atmosphere of a relative humidity of 100 percent at 20 degrees C.. Compressive strength test was based on JIS A 1108.

Setting test

The setting test was based on JIS R 5201-1992 of the cement setting test. Admixture samples were BS, ST, W and Ca. The admixture substitution rate was inner 30 percent of OPC.

Hydration exotherm rate measurement

Hydration exotherm rate was measured by the twins-type conduction calorimeter. The admixture was BS, ST, W and Ca. An admixture substitution rate was inner 30 percent to OPC, and water-binder ratio was 100 percent. Measurement was continued until the second exothermal peak appeared after stabilized at 20 degrees C..

Results and discussion

Evaluation of volume stabilization

Free lime content

Free lime content of the converter slag is shown in fig.1 and fig.2. The free lime content of specimen without treatment was about 3.5 percent when the grain diameter is 2.5 and 0.15 millimeters, and was about 2.5 percent in the other grain size. With the heart treatment, the free lime of the converter slag was remarkably reduced 30 percent at a specimen with a grain diameter of 2.5 millimeters, and 20 percent at a grain diameter of 0.15 millimeters. The same tendency was observed in the other treatment such as immersion in water and in $Ca(OH)_2$ aqueous solution. They decreased less than 2 percent by the immersion for 1 day that is the critical free lime content for an expansion risk[5] but no further decrease was observed until immersion 7 days.

State of ferro oxidizes on the surface of the converter slag

State of ferro oxidizes on the surface of the converter slag specimens without treatment(ST) and with heating treatment(B) were measured with XPS and is shown in table.3. FeO which is expansion factor occupies 30% on the surface of the converter slag of ST. After the firing treatment, 9% in FeO changed with FeO to FeOOH, Fe_2O_3.

Identification of the principal mineral

A XRD patterns about the converter slag without treatment(ST), with heating (B) and with immersion in water (W) are shown in fig.3. CaO, $CaCO_3$, $Ca(OH)_2$, beta-C_2S, C_2F, FeO and $Fe(OH)_3$ were detected in ST.

Length change measurement

Length change of specimen with a substitution of 70 percent is shown in fig.4. While PL and BS showed contraction specimens with converter slag showed expansion. Expansion order was ST>W>Ca. The expansion of the specimens with converter slag showed maximum at the was age of 14 days (7 days after mixing), a subsequently, ST and W contracted after the age of 14 days, and became nearly constant after the age of 56 days. Ca became nearly a constant after the age of 14 days, and the contraction became equivalent to ST and W after the age of 56 days. Expansion magnitude of Ca by the age of 14 days was about 30 percent of ST, 45×10^{-6}. Therefore, the expansion due to free lime and FeO can be reduced when specimens are immersed the Ca $(OH)_2$ aqueous solution and heated at a low temperature.

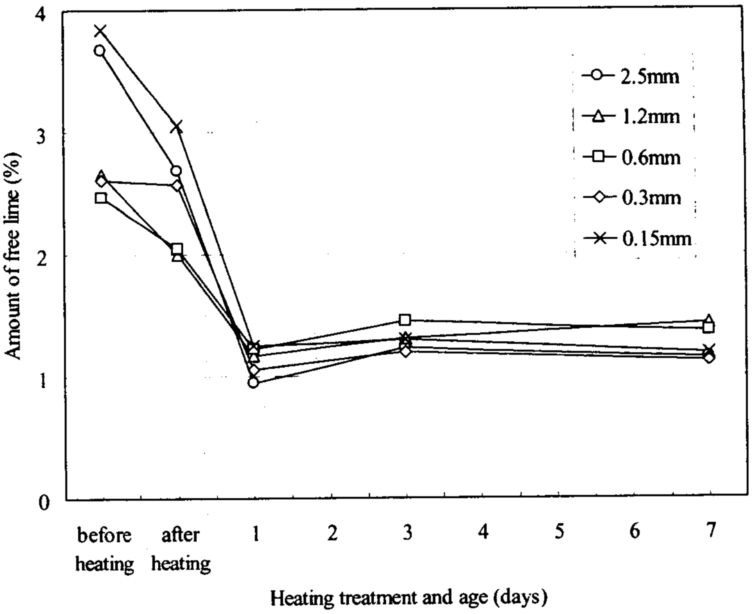

fig.1 Free lime content of converter slag before and after heating , and after immersion in water

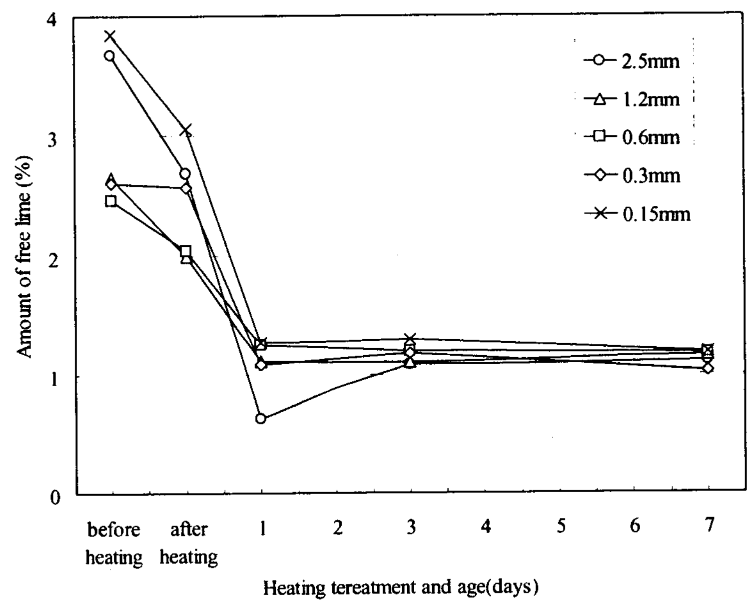

fig.2 Free lime content of converter slag before and after heating , and after immersion in $Ca(OH)_2$ aqueous solution

table.3 State of ferro oxidizes on the surface of the converter slag

	FeO	FeOOH	Fe_2O_3
before heating	29.45	26.40	44.15
after heating	20.32	28.19	51.49
Increase and decrease	-9.13	1.79	7.34

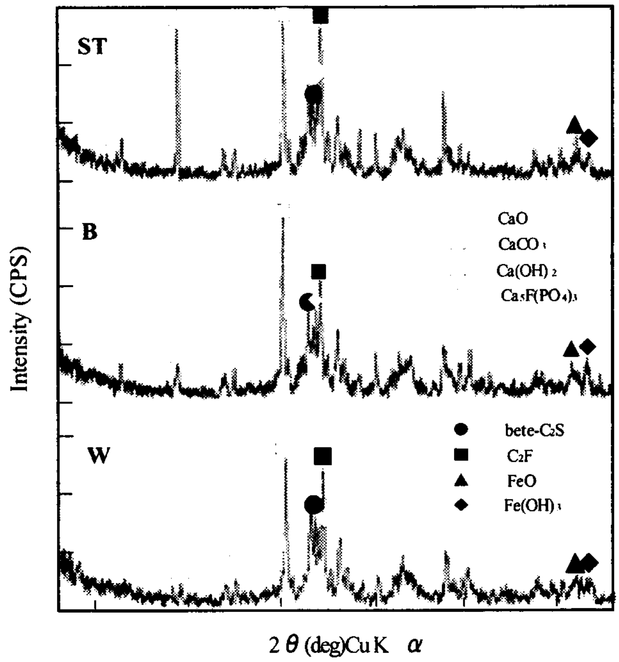

fig.3 XRD patterns about the converter slag

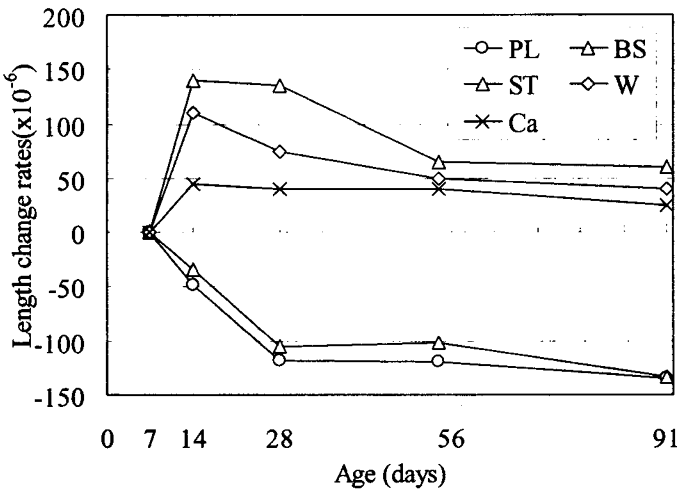

fig.4 Length change of specimen with a substitution of 70 percent

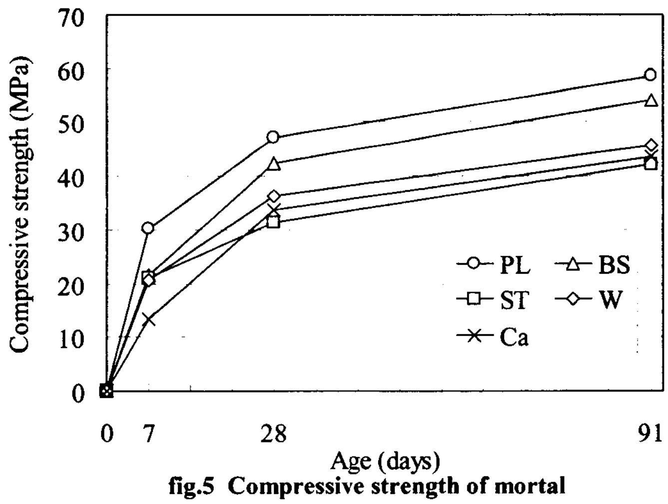

fig.5 Compressive strength of mortal

Evaluation as an admixture

Compressive strength test

Results of the compressive strength test of PL, BS, ST, W and Ca are shown in fig.5. BS, ST and W showed equal strength at the age of 7 days, but the strength of Ca was about 25 percent of that of BS. In the normal hydration, Ca^{2+} may elute form OPC. However in the converter slag – water system, $Ca(OH)_2$ remains in the converter slag may control the Ca^{2+} elution. Therefore, the generation of C-S-H was disturbed resulting in a low strength. The strength of BS was about 90 percent of PL at the age of 28 days, while specimens with the converter slag showed equal strength. Especially, increase in strength of Ca until 28 from age 7 days was about two times greater than ST and W. The strength of ST, W and Ca was equal, and became about 80 percent of PL and BS at the age of 91 days. Therefore, it was found that, though initial strength decreases in comparison with BS, increase in strength of the converter slag at ages from 7 days to 28days is bigger than BS. This may be attributed to the followings. It is confirmed that considerable Al is contained in C_2F in the converter slag. This C_2F and gypsum may react, and form Ettringite.[2] Therefore, it is expected that the C_2F contained in the converter slag forms a C_4AF-type mineral containg Al and Fe. The hydration reaction of C_4AF is quicker than that of beta-C_2S, and therefore C_4AF selectively reacts with the gypsum in OPC forming the Ettringite leading to the increase in strength at the age from 7 to 28 days.

Setting test

Results of the setting test are shown in fig.6. The initial setting time was retarded in an order of OPC=BS=Ca>W>ST, and the final setting time was retarded in an order of Ca>OPC=BS>ST=W. OPC and BS behaved similarly. The initial setting time of Ca was equal to those of OPC and BS, and final setting time was quicker than those of OPC and BS. This may be attributed that $3CaO \cdot Al_2O_3$ (C_3A) mineral in OPC reacted with $Ca(OH)_2$ and formed hydrates rapidly, resulting in a promotion of setting.

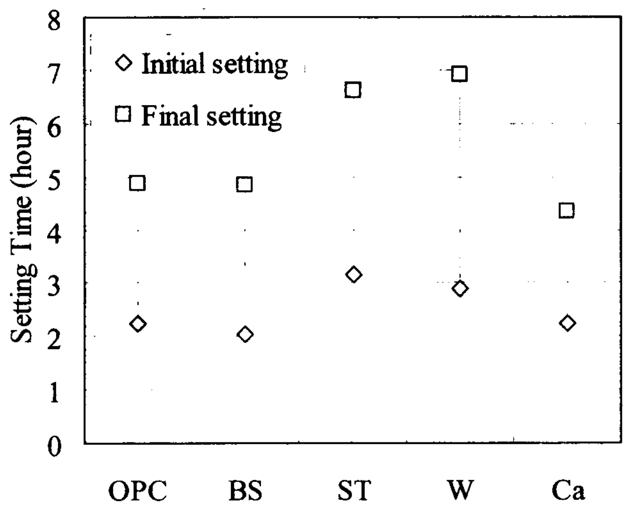

fig.6 Results of the setting test

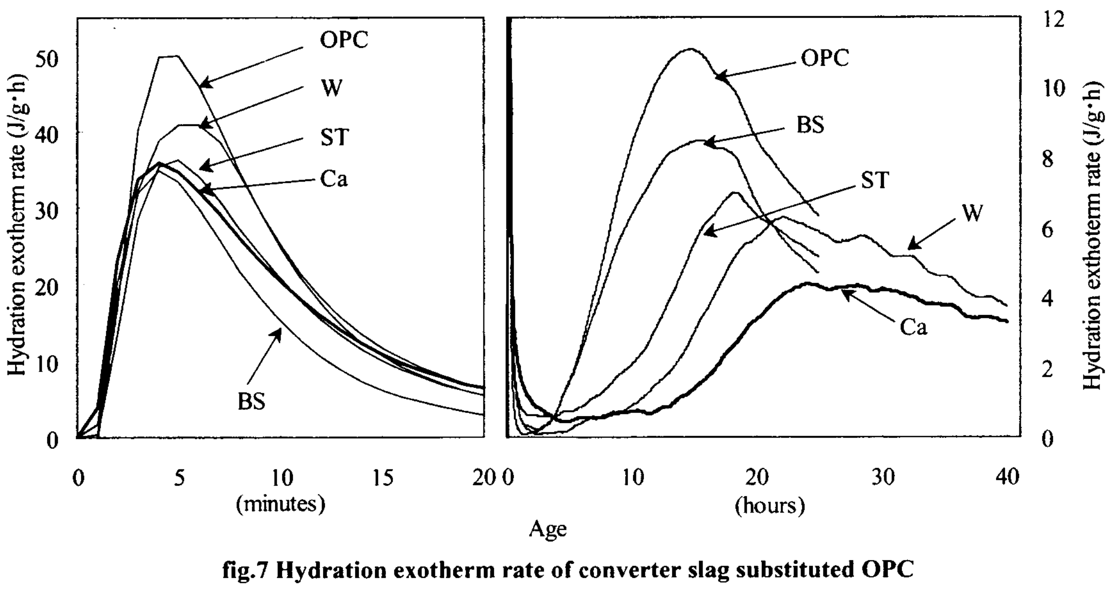

fig.7 Hydration exotherm rate of converter slag substituted OPC

Hydration exotherm rate measurement

Hydration exotherm rate of converter slag substituted OPC is shown in fig.7. The hydration exotherm rate of the converter slag was smaller than that of OPC in the first and the second peak for all the specimens including BS. The first peak of the converter slag show greater hydration exotherm than that of BS. This may be attributed to the free lime in the converter slag that may still be remaining. The second exothemal peak of the converter slag was lower than of OPC and BS, and was about 50 percent of that of BS and about 40 percent of that of OPC. The peak occurrence delayed 15 hours in comparison with OPC. A converter slag can be expected to have an effect in reducing the hydration exothermic heat.

Conclusions

We aimed to stabilize the converter slag which had self-disintegration and examined the use as a concrete admixture. The followings are confirmed in our test.

Free lime in the converter slag with a of grain diameter from 0.15 millimeters to 5 millimeters was able to be reduced as low as 1 percent by the heating at 450 degrees C. for 2 hours and by the water (aqueous solution) immersion treatment.

FeO on the surface of the converter slag was able to be reduced as low as 10 percent by the heating at 450 degrees C. for 2 hours.

When the converter slag is stabilized by heating and the immersion in $Ca(OH)_2$ aqueous solution, the length change rates of the mortar substituted 70 percent with the stabilized converter slag decreased for 70 percent of that of the control specimen, and the maximum expansion magnitude was 45×10^{-6}.

The compressive strength of the mortar, inner 30 percent of OPC., was 80 percent of that of OPC at the age of 91 days, and the increase in compressive strength of the mortar showed maximum at an age from 7 to 28 days.

Effect on the acceleration of setting was confirmed when the converter slag is treated in $Ca(OH)_2$ aqueous solution.

A converter slag can be expected to have an effect in reducing the hydration exothermic heat.

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Appendix

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