The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Properties of reduced and quenched converter slag

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Abstract

Converter slag has some compositional similarities to portland cement. But it has no hydration properties due to it's quite high concentrations of FeO(20-35%), MnO(4-6.5%) . So it is needed to reduce the concentrations of iron and manganese of converter slag to use as cement additives by enhancing it's hydration properties.

In this study, converter slag was modified it's composition by mixing of silica, alumina and quenched BF slag and reduced in induction furnace and quenched in running water. The hydraulic properties and structures of modified and quenched converter slag are significantly changed depend on the amount and kinds of additives. The addition of alumina up to 10% and BFQ slag up to 20% by weight on converter slag was effective to enhance the hydraulic properties of modified and quenched slag.

The addition of reduced and quenched converter slag up to 20% by weight in replacement of portland cement in mixing of concrete mortar were shown higher compressive strength than 100% cement concrete mortar.

Key words : converter slag, reduction, water quenching, hydration, cement additives

1. Introduction

The low contents of CaO and high contents of FeO, MgO and MnO of the slag are the major difference between steel slag and portland cement. Because of the high iron and manganese contents of steel slag, the existing cement kiln can only accept converter steel slag up to 10% of the total raw materials during the clinkering process. As a result of systematic and intensive research for steel slag, new fields of application have been developed.

S. Kubodera et al. suggested the methods of the full utilization of LD slag that consists of the reduction of molten LD slag by coke in an electric furnace to separate it into slag and metal, and the further treatments of the slag and metal thus obtained to make cement, fertilizer, iron sand and steel. But it couldn't be industrialized because of the complexities of component processes.(1)

One research has shown that, by changing the iron valence from Fe^{2+} to Fe^{3+}, the hydraulic potential of steel slag (defined as reactivity of slag towards water and capability of developing high compression strengths) can be much improved due to the enhanced glass forming capability of the molten slag.

One of the authors has been made an attempt to enhance the cementitious nature of the steel slag by oxidizing the iron in the slag to the highest oxidation state, primarily trivalent, and by quenching the slag to form a partial glass. This allows the material to be blended with portland cement (at additions up to 20% by weight) , without affecting the strength and performance of the material.

If the converter slag is reduced and it's composition could be changed to enhance it's hydraulic potential by water quenching. It could be used as cement additives or raw materials for slag cement making like as BFQ slag. In this study, the authors were trying to understand the change of phases and the behavior of the hydraulic properties of reduced and quenched converter slag on the composition change.

2. Experiments

2.1 materials

Table 1. Composition of BOF slag and BFQ slag and four components Basicity

(wt %)

	CaO	SiO_2	MgO	Al_2O_3	Fe_2O_3	MnO	Basicity
BOF slag	33.79	10.94	8.16	0.84	35.25	6.83	3.6
BFQ slag	35.86	37.24	12.61	8.83	2.1	1.32	1.1

Table 1. shows the compositions of slag used in this study. The four components basicities of BOF slag and BFQ slag are 3.6 and 1.1 each other. The main phases of BOF slag are $2CaO \cdot SiO_2$ and Wüstite solid solution. BFQ slag is a complete glass.

2.2 experiments

Sample preparation was done by using a 15kw RF Induction furnace which was set graphite susceptor and cduld keep reduction atmosphere. Some amount of converter slag were mixed with predetermined percentage of silica, silica+alumina, quenched BFQ slag and active carbon. Reduction and modification melting was carried out using carbon-clay crucibles at 1650°C. The melts were quenched in running water. Metallic Iron was separated from slag. The modified and quenched slags were analyzed by SEM-EDX and XRD. The heat of hydration of quenched slags were also measured by Isothermal conduction calorimeter at 60°C for 24hours.
Also three different types of modified slags (10%SiO2 added, 5%SiO2+5%Al2O3 added, 10%Al2O3 added) were prepared and grounded to −150 μm and blended with portland cement to investigate the change of the compressive strength of slag mixed concrete mortars.

3. RESULTS AND DISCUSSION

3.1 phase changes of the reduced and quenched BOF slag

The phases of modified BOF slags were changed on the kinds and the amount of additives. These phase changes investigated by XRD and SEM-EDX are summarized in Table 2.

Figure 1 is the XRD and SEM-EDX of 5%SiO2+X%Al2O3 slag system. As can be seen in this figure, the main phase of these slags are changed from (Larnite + free MgO) to (Bredigite + free MgO + Glass) as the increase of alumina. Also the glass phase is increased at higher alumina contents. The main peak intensity near $2\theta=43°$ of Periclase(free MgO) becomes sharp and intensified as the increase of alumina addition.

The XRD and SEM-EDX of X%BFQ slag system is shown in Fig. 2. This figure shows the main phase of 10%~30% BFQ slag is Larnite + free MgO which is very similar to 5S5AQ.

The XRD of 40BFQ is similar to that of 5S10AQ. The main peak intensity of Periclase (free MgO) becomes intensified as the increase of BFQ slag addition as well as the 5%SiO2 + X%Al2O3 slag system.. Free MgO (Periclase) can be seen as dark glassy phase at 30BFQ slag as shown in Fig. 3.

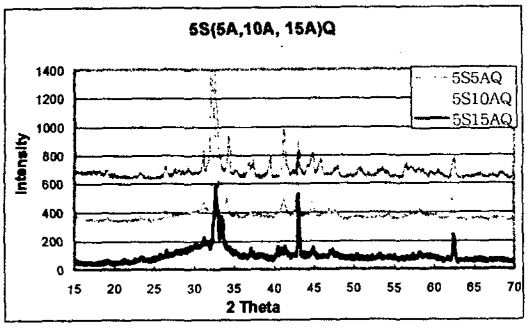
Free MgO (Periclase) phase was only detected in the samples of 5%SiO2+X%Al2O3 and X%BFQ slag added, reduced and quenched. These two slag systems have similar mineral structure of Larnite+free MgO.

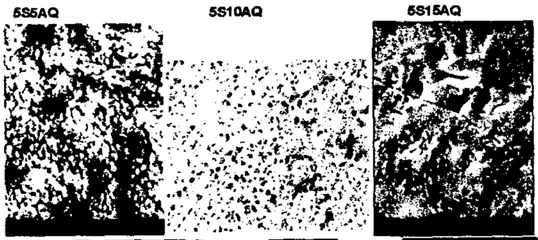
Figure 4 is the XRD of X%SQ slag. 10SQ has larnite main phase, it's XRD pattern is similar to 5S10AQ and 40BFQ but shows no free periclase peaks. 15SQ and 20SQ are merwinite which is 3CaOMgO2SiO2

Table 2. Main phases of head slag and various kinds of reduced and quenched BOF slag

BOF slag	C_2S, Wüstite solid solution
BFQ slag	Glass
10SSC	Bredigite($CaO_{1.7}MgO_{0.3}SiO_2$), Merwinite(C_3MS_2)
20SSC	Akermanite(C_2MS_2)
30SSC	Akermanite
10SQ	C_2S, Larnite
15SQ	Merwinite
20SQ	Merwinite
5S5AQ	L+ free MgO+ Glass
5S10AQ	L+B+free MgO+Glass
5S15AQ	B+free MgO+Glass
10S5AQ	Merwinite
10S10AQ	Merwinite
10S15AQ	Glass
10BFQ	C_3S, C_2S,
20BFQ	Larnite+free MgO
30BFQ	Larnite+free MgO
B: Bridigite, L: Larnite	

10SSC : 10%SiO_2 added and slow cooled
10SQ : 10%SiO_2 added and quenched
10BFQ : 10%BF slag added and quenched
5S5AQ : 5%SiO_2+5%Al_2O_3 added and quenched



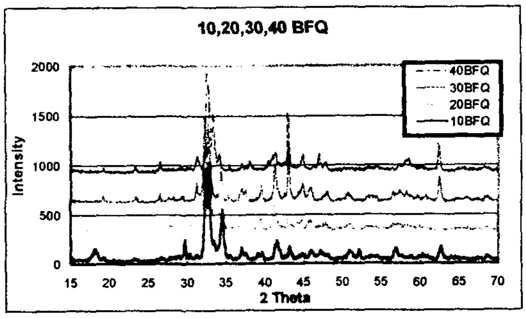


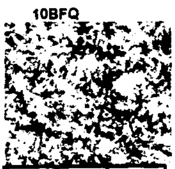
	Matrix	white dot
CaO	58.2	50.2
SiO2	27.5	28.4
Al2O3	7.4	11.7
MgO	6.9	9.7

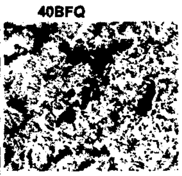
	Matrix
CaO	53.1
SiO2	19.9
Al2O3	12.9
MgO	11.3
MnO	1.3
TiO2	0.9
S	0.6

	Matrix	small dot
CaO	40.3	44.1
SiO2	27.1	24.8
Al2O3	21.3	25.3
MgO	11.3	4.8
TiO2	**	1

Fig. 1 XRD and SEM-EDX of 5%SiO_2+X%Al_2O_3 added BOF slag







Matrix	CaO	69.0
	SiO2	22.7
	Al2O3	2.6
	MgO	4.3
	TiO2	0.6
	SO4	0.8
		C2S
white flower	CaO	78.1
	SiO2	14.8
	Al2O3	4.7
	MgO	2.4
		C3S

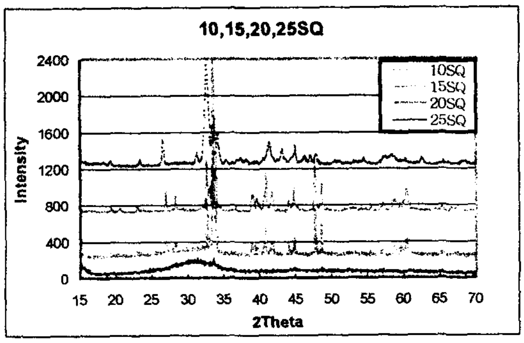
	Matrix	White area
CaO	54.5	58.9
SiO2	27.8	30.6
Al2O3	10.8	6.1
MgO	6.9	4.4

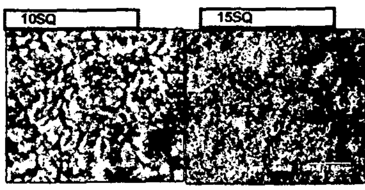
	Glassy	Porous
CaO	58.8	59
SiO2	19.5	23.8
Al2O3	5.6	2.4
MgO	10.5	12.2
SO4	3.1	1.6
TiO2	1.9	0.9
MnO	0.6	***

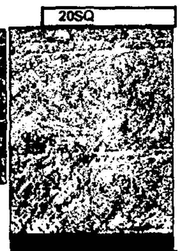
Fig. 2 XRD and SEM-EDX of X%BFQ slag added BOF slag

	Dark Glassy	Cracked Matrix
CaO	1.1	61.0
SiO_2	***	30.4
Al_2O_3	***	2.8
MgO	98.7	4.8
MnO	0.2	***
	MgO	C_2S(Larnite)

Fig. 3 SEM Photo and EDX of 30% BFQ slag added BOF slag







10SQ	Matrix
CaO	65.50%
SiO2	28.30%
MgO	4.30%
Al2O3	1.90%

15SQ	Matrix
CaO	52.9
SiO2	32.9
MgO	8.7
SO4	0.8
MnO	3.6
TiO2	1.1

20SQ	Matrix
CaO	43.3%
SiO2	41.6%
MgO	11.4%
Al2O3	0.6%
MnO	1.8%
TiO2	0.8%

Fig. 4 XRD and SEM-EDX of X%SiO_2 added BOF slag

3.2 Heat of Hydration of modified slags

Table 3. Heat of Hydration of modified slags (no activator added)

Sample	Heat of Hydration(J/g)	state
Port. Cement	322.1	set
5S5AQ	178.3	set
5S10AQ	84.3	set
10S5AQ	31.2	set
10S10AQ	24.7	set
10S15AQ	10.1	wet
10SQ	48.5	set
15SQ	22.6	set
20SQ	0.7	crumbles
25SQ	0.5	crumbles
10BFQ	143.2	set, swell
20BFQ	141.7	set
30BFQ	84.1	set

The heat of hydrations of 4 different types of modified slags were summarized in table 3. Portland cement was chosen as a reference material for contrasting the behavior of modified steel slags. All samples showed a calorimetric curve typical of C3A or C4AF which have two exothermic peaks, first one is due to the wetting of the sample and second peak is due to the setting.

The heat of hydrations of 5S5AQ, 10BFQ and 20BFQ are quite high compare to the other slags. The main phases of these slags are C_2S (Larnite)+freeMgO and showed very good setting in hydration reaction. On the other hand, the other slags of which main phases are Merwinite or Glass such as 20SQ, 25SQ and 10S15AQ released low heat of hydration and resulted no settings.

3.3 Compressive strength of modified slag mixed cement mortars

Three types of modified slags, 10%SiO2 added, 5%SiO2+5%Al2O3 added and 10%Al2O3 added, were mixed in relacement of cement from 10% to 30% of cement to make concrete mortars. Also as a reference, 100% cement concrete mortar was fabricated. The size of mortar was Φ50mm×H100mm. The compressive strength of mortars were tested in Instron at a cross head speed of 0.2mm/sec. The results of these tests were shown in Fig. 5 ~ Fig. 7. As can be seen in these figures, alumina added slag mixed mortar and alumina+silica added slag mixed mortar showed higher compressive strength than 100% cement mortar.

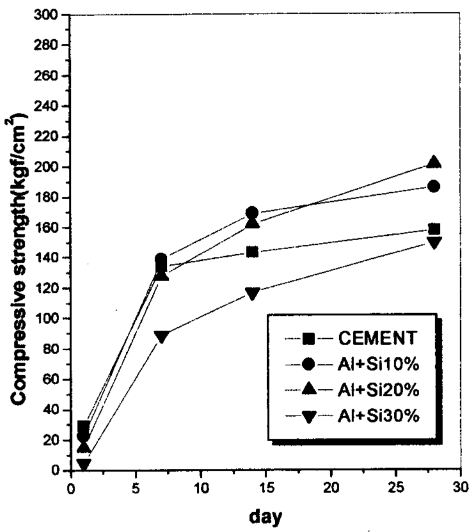


Fig. 5 Compressive strength of cement concrete and quenched 5S5A slag added mortar (cement, CAS10, CAS20, CAS30)

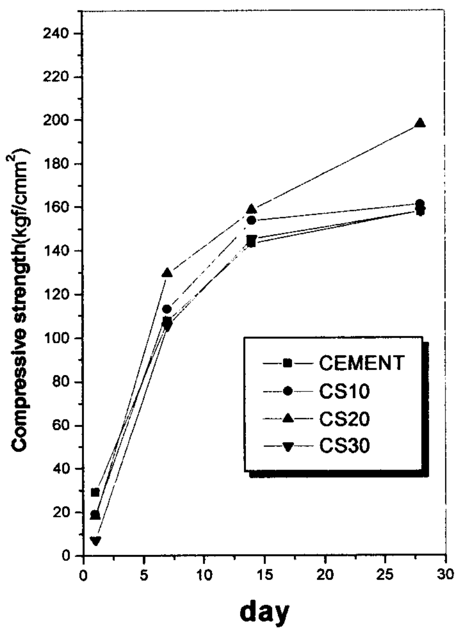


Fig. 6 Compressive strength of cement concrete and quenched 10S slag added mortar (cement, CS10, CS20, and CS30)

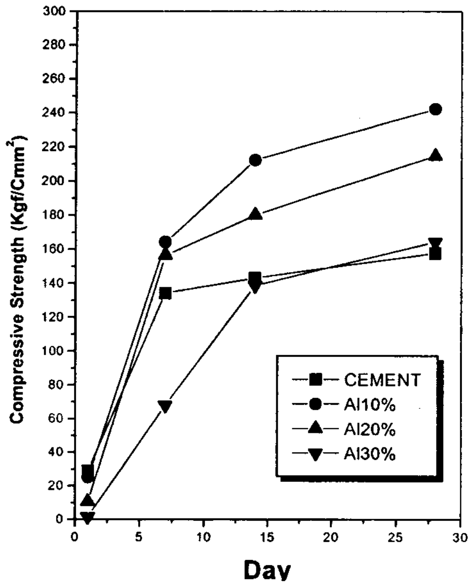


Fig. 7 Compressive strength of cement concrete and quenched 10A slag added mortar (cement, CA10, CA20, and CA30)

4. Conclusion

Converter slag was modified it's composition by mixing of silica, alumina and quenched BF slag and reduced in induction furnace and quenched in running water.

The hydraulic properties and structures of modified and quenched converter slag are significantly changed depend on the amount and kinds of additives. The addition of alumina up to 10% of slag and BFQ up to 20% of slag on converter slag was effective to enhance the hydraulic properties of modified and quenched slag.

The addition of reduced and quenched BOF slag up to 20% by weight in replacement of Portland cement in mixing of concrete mortar were shown higher compressive strength than 100% cement concrete mortar.

5. References

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Acknowledgement

One of the authors would like to acknowledge financial support received from Institute of the development of advanced materials, Chonbuk National University.
Part of this work was done at the Department of Metals and Materials, The University of British Colombia, Canada