

POZZOLANIC REACTIVITY AND COMPRESSIVE STRENGTH OF GASIFIED COAL SLAG ADDED WITH LIMESTONE FLUX

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INTRODUCTION

In recent years, an entrained flow gasification of coal, which has several advantages over other gasification processes including high throughput per reactor volume and flexibility in coal types, has attracted special interest in many countries. The gasifier involves wet ash removal. The liquid slag formed has suitable viscosity for tapping and is withdrawn at the bottom of the reactor without promoting the corrosion in the reactor insulation. To operate the gasifier stably and to maintain high gasification efficiency, it is necessary to control ash melting temperature by adding limestone which causes decrease in ash melting temperature and slag viscosity(1). The use of the slag/lime mixture as a partial replacement in slag portland cements is of interest, because of utilization of waste slag. Slag portland cements with higher slag contents are used for mass concrete because of their low heat evolution. And those with lower slag content are used as a substitute of portland cement. Japanese Industrial Standard (JIS) has permitted the addition of slag or other latent hydraulic or pozzolanic materials to the portland cements.

In this paper, characterization on coal gasification slag loaded with limestone additive obtained from a laboratory-scale entrained bed gasifier was performed in order to obtain the relation between the character of the glass phase, pozzolanic reactivity and compressive strength of the blending component.

EXPERIMENTAL

Two sorts of Blair Athol slag, gasified slag A and B, were obtained from a laboratory-scale entrained bed gasifier(2). Limestone was added to the coal as a flux to control operation temperature of the gasifier. The CaO content of the slag was relatively high and, therefore, the melting temperature of the slag was much lower than that of original slag. Important characters of the slag are shown in Table 1.

Infrared spectrum of ν_2 stretching vibration of Si-O bond in slag was measured by FT-IR method. 30% Ca(OH)₂ and 10% CaSO₄·2H₂O as activator were added to each slag. The slag was mixed with water solid ratio of 0.5 and cured at 313K for 1, 7 and 28 days. Hydration reactivity of the blending component was evaluated from its hydration degree, amount of combined water and reacted Ca(OH)₂. Hydration degree of the blending component was determined by XRD after heating and recrystallizing hydrated sample at 1273K for half an hour. Amount of combined water and reacted Ca(OH)₂ was measured by ignition loss and TG method, respectively(3). Compressive strengths of the blending component and the slag cements containing 25 to 75wt% of portland cement were measured in conformity to the JIS (Japanese Industry Standard) method.

RESULTS AND DISCUSSION

Condensation Degree of Silicate Ions in Glass Phase

Most slag and melted ash are more complex than vitreous SiO_2 . Glass phase results from co-melting silicate with other oxides, some of which provide elements with coordination numbers generally of 3 or 4 (e.g. Al, Fe, etc.), which are capable of replacing Si in the polymeric network, known as network modifiers(4). As CaO is introduced into a silica melt, the resulting slag formed on quenching became increasingly depolymerized, relative to the parent coal slag.

The averaging phenomena for heterogeneous assemblages of melted glass phase containing CaO was observed by the FT-IR method. Typical infrared spectra of ash-CaO mixture slag showed a number of characteristic bands which are seen to vary with the origin of the slag, which can be compared with other similar mineral species. It is well known that ν_3 stretching vibration of Si-O bond makes strong absorption at 1100cm^{-1} in IR spectrum and this absorption peak shift towards high wave number as the condensation degree of silicate ions increases(5). The peak position each slag component by IR is shown in Figure 1. Gasified slag A and B and blast furnace slag had a peak at about 950 to 940cm^{-1} . While Blair Athol slag and fly ash had a peak at about 1060cm^{-1} . The condensation degree became larger in the order of high calcium slag.

Pozzolanic Reactivity of Slag

The amount of combined water and reacted Ca(OH)_2 and hydration degree are shown in Figure 2. Since the glass phase has higher level of free energy than the crystalline phase, the glass phase is corresponded with the reactivity of the blending component more deeply. Content of glass phase in slag was above 99%. Hydration degree and combined water of the gasified slag B were almost equal to those of the blast furnace slag at 28 days. Those of the gasified slag A with less than 1% crystalline phase, however, were small. The pozzolanic reactivity of slag is considered to correspond to CaO content and the condensation degree of silicate ions, i.e. a network with a lower degree of connectivity. On the other hand, amount of reacted Ca(OH)_2 could not be estimated in case of slag rich in CaO.

Compressive Strength of Slag

Figure 3 shows the compressive strength of the blending component. As expected, blast furnace slag and gasified slag B gave the highest strength development after 28 days. However, gasified slag A resulted in significantly lower strength due to the low pozzolanic reactivity.

The effect of portland cement content on the compressive strength developed by the slag shows in figure 4 and 5. Blending cements containing 25wt% of the slag/75wt% portland cement show higher strength from 7 days onwards. The strengths of the gasified slag B cement were found to exceed the JIS value. The improved strengths are more likely to be due to the speeding up the pozzolanic reaction.

CONCLUSIONS

The pozzolanic reactivity of the slag was enhanced with increasing basicity and CaO content in slag and decreasing of the degree of condensation of silicate ion in the glass phase. Hydrated products from the slag cement were not basically different from those from blast furnace slag cement. The compressive strength of high calcium slag cement (gasified slag B) was almost equal to that of blast furnace slag.

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Table 1 Characteristics of slags used in this study

		Gasified slag A	Gasified slag B	Blast furnace slag	Fly ash
SiO ₂	(%)	46.5	39.46	32.67	54.10
Al ₂ O ₃	(%)	21.68	14.61	12.43	21.03
Fe ₂ O ₃	(%)	2.12	2.94	0.56	4.71
CaO	(%)	17.34	35.56	44.50	10.41
MgO	(%)	0.24	0.32	5.56	1.24
ST	(K)	1610	1540	-	-
HT	(K)	1660	1580	-	-
FT	(K)	1700	1610	-	-
C/S		0.37	0.90	1.36	0.19
(C+M)/S		0.38	0.91	1.53	0.22
(C+M)/(S+A)		0.26	0.66	1.11	0.16
(C+M+A)/S		0.84	1.28	1.91	0.60
Content of glass phase (%)		0.99	0.99	0.99	0.70

A:Al₂O₃, C:CaO, M:MgO, S:SiO₂

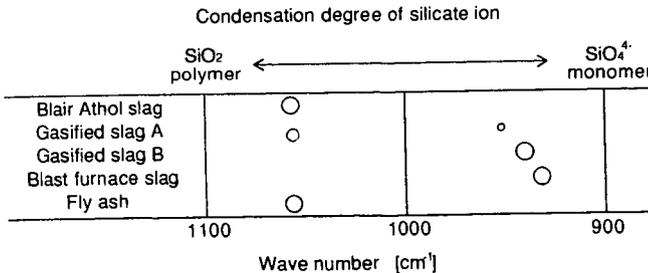


Figure 1 Peak position of infrared absorption spectrum of blending component 2012

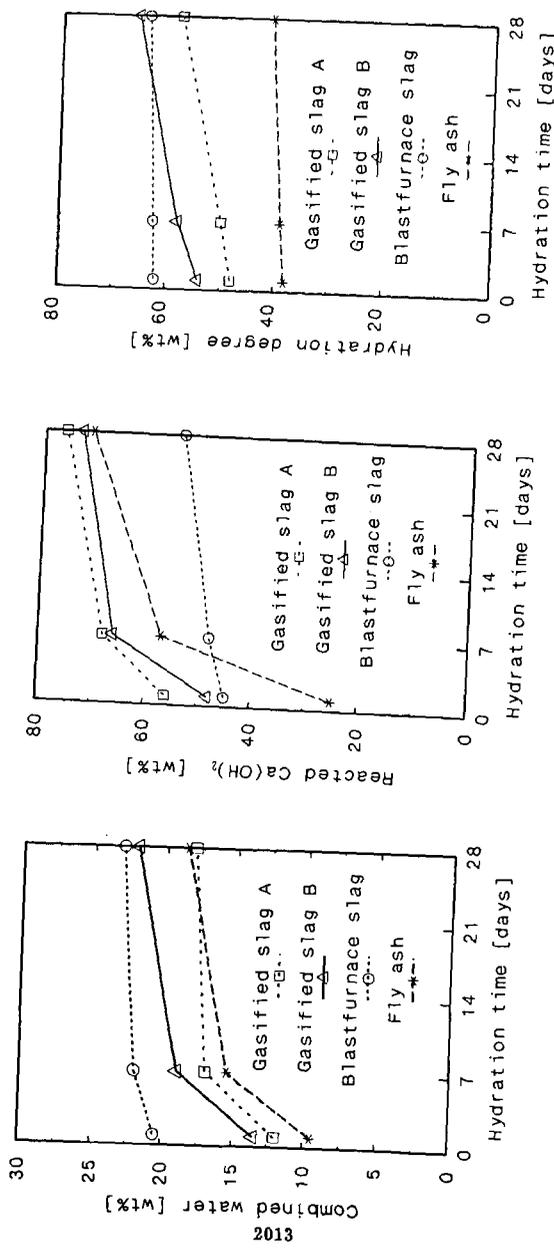


Figure 2 Amount of combined water, reacted $\text{Ca}(\text{OH})_2$ and hydration degree of blending component with hydration time (313K)

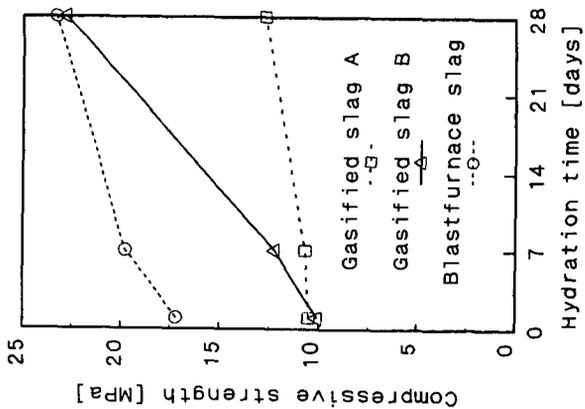


Figure 3 Compressive strength of blending component with hydration time

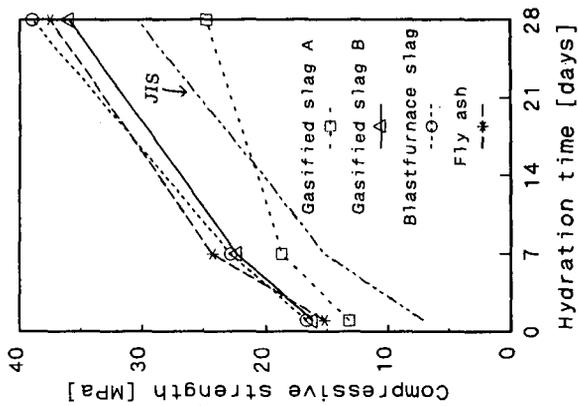


Figure 4 Compressive strength of slag cement containing 75wt% portland cement with hydration time

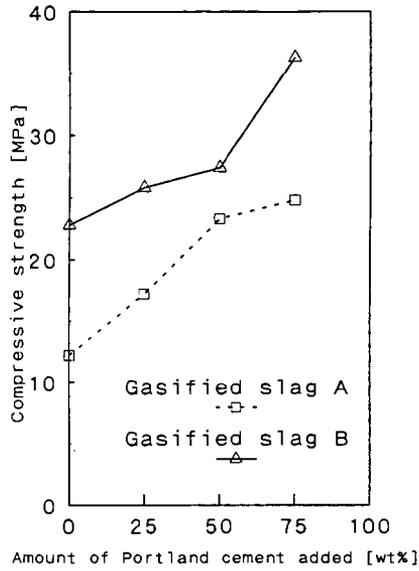


Figure 5 Effect of portland cement content on the compressive strength developed by the slag