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Calorimetric study on hydration of CaO-based oxides

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Abstract

Hydration behavior of compounds in Ca–(Si, Al or Fe)–O systems, CaO–(FeO or MnO) solid solutions and various kind of slags were investigated using calorimetric and dilatometric techniques in order to clarify the effects of CaO-based oxides on stability of steelmaking slag. Slow hydration rate and large volume expansion were observed in $3CaO \cdot Al_2O_3$, which was a harmful component for stabilizing slag. Heat of hydration and volume expansion of CaO solid solutions were almost the same as those of pure CaO in lower solute content region than 30-mole%, while the hydration rate decreased as MnO contents increased in higher solute content region. Hydration behavior of converter slag was dominated by free lime contained in the slag. It was suggested that $3CaO \cdot Al_2O_3$ affected hydration behavior of ladle furnace free (LF) slag because Al dissolution was detected after calorimetric measurements and slow expansion rates and higher heat of hydration than that calculated with free lime contents were observed for LF slag. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heat of hydration; Slags; Calorimetry

1. Introduction

Hydration is one of the most important steelmaking slag properties for the utilization because it relates to element dissolution and volume expansion. Sufficient volume stability is required in utilizing steelmaking slag as road construction materials. It is well known [1–6] that the volume expansion of slag is mainly caused by hydration reaction of free lime in the slag represented by Eq. (1)

$$CaO(s) + H_2O(l,g) = Ca(OH)_2(s). \tag{1}$$

Recently, a steam-aging technique has been employed to stabilize the free lime before utilizing steelmaking slag [7–10]. The volume expansion of slag is required to be less than 1.5% for road construction [11]. Therefore, hydration behavior of slag components should be clarified in detail in order to extend the utilization of steelmaking slag. The important components in steelmaking slag for volume expansion are CaO-based compounds and free lime which forms solid solution with divalent metal oxides (MnO, FeO and MgO) [1,2]. However, the effects of CaO-based compounds and CaO solid solutions on hydration of steelmaking slag have not been revealed in detail.

Since Eq. (1) is an exothermic reaction, calorimetry can be an effective method to provide information on hydration reaction of the CaO-based oxides. In the present work, heat of hydration and volume expansion have been measured for CaO-based compounds, CaO solid solutions and slags, and effects of CaO-based oxides on hydration of steelmaking slag are discussed.

2. Experimental

2.1. Test samples

Synthetic conditions for CaO-based oxides and chemical composition of slags are listed in Tables 1 and 2, respectively. The CaO-based oxides were synthesized by a solid phase sintering method using $CaCO_3$, Al_2O_3, Fe_2O_3, SiO_2, CaO, MnO and FeO powders as source materials. β-2CaO·

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Table 1
Synthetic conditions of CaO-based oxides

Oxides	Temperature (K)	Time (h)	Atmosphere
$2CaO \cdot SiO_2(\beta)$	1773	3	O_2
$2CaO \cdot SiO_2(\gamma)$	1773	3	O_2
$3CaO \cdot SiO_2$	1873	3	O_2
$2CaO \cdot Fe_2O_3$	1473	3	O_2
$3CaO \cdot Al_2O_3$	1673	3	O_2
$12CaO \cdot 7Al_2O_3$	1473	36	O_2
CaO–8.1~44.1mol.%MnO	1473	24	Ar
CaO–8.0~12.1mol.%FeO	1473	24	Ar

SiO_2 was stabilized by alumina (0.6mass%) [12]. Free lime contents listed in Table 2 were determined by the ethylene glycol extraction method. All of the slags were obtained during actual operation.

2.2. Calorimetric measurement

Fig. 1 shows a schematic diagram of the Tian–Calvét type twin calorimeter employed in the present experiments. Two cells, working and reference, were located in a stainless steel (SUS316) block held at constant temperature. In each of these twin units, a temperature difference between the cell and the constant temperature block was detected with 96 couple thermopile as an electromotive force [13,14].

The sample for calorimetric experiments, CaO-based oxide or slag, was ground, weighed and charged into a gelatin capsule in a glove box. After the temperature of the stainless steel block was stabilized at 327 K, the sample with a gelatin capsule was dropped into distilled water, solvent, in the working cell to measure the heat of hydration. The enthalpy change of reaction of the sample with distilled water was defined as the heat of hydration. The solvent was stirred with a glass rod to accelerate the hydration reaction. The heat of reaction of the gelatin capsule with distilled water was measured and used in correction for heat of hydration of the sample. The calorimeter was calibrated electrically. After completion of the calorimetric measurements, the solvent was chemically analyzed by induction coupled plasma (ICP) atomic emission spectroscopy. The samples after hydration were examined by X-ray diffraction (XRD) (Ni-filtered, CuKα).

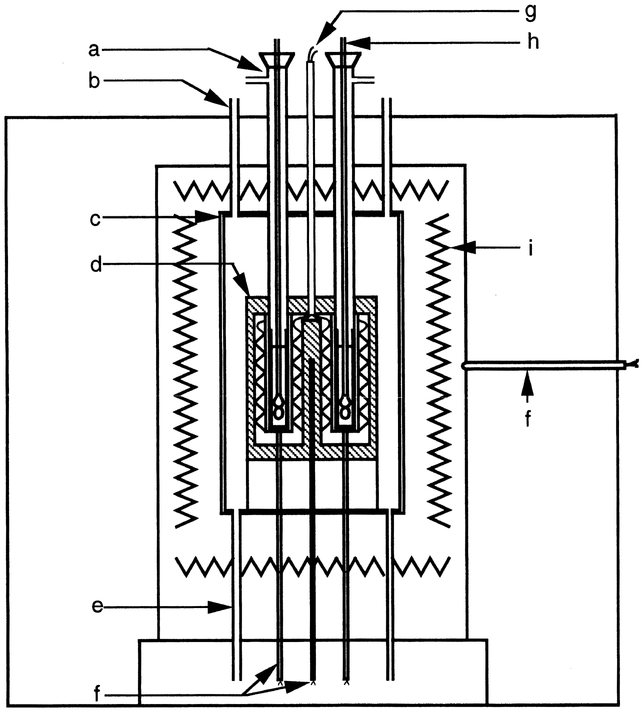

Fig. 1. Schematic diagram of Tian–Calvét type twin calorimeter. (a) glass tube; (b) N_2 gas inlet tube; (c) heavy shield; (d) stainless steel block; (e) N_2 gas outlet tube; (f) thermocouple; (g) thermopile lead wire; (h) stirring rod; and (i) heater.

2.3. Expansion test

Sample powder was pressed into disks (25 mm in diameter and 5 mm in thickness), and then volume expansion of the disk in water of 353 K was measured continuously with a dilatometer [15]. The total expansion test time was 240 h.

3. Results and discussion

3.1. CaO-based compound

Fig. 2 shows enthalpy change for hydration of CaO-based compounds (ΔH_{327}) as a function of the amount of the CaO-based compound (M_{comp}) dropped into distilled water. The heat of hydration per mole of CaO in the compound (ΔH_{comp}) can be calculated assuming the linear

Table 2
Chemical composition of slags

	Chemical composition (mass%)									
	CaO	SiO_2	Al_2O_3	MgO	MnO	P_2O_5	T.Fe	TiO_2	CaF_2	Free CaO
Blast furnace slag	42.8	33.9	13.1	6.45	0.35	0.013	0.43	0.53	–	0.5
Converter slag A	51.6	9.0	1.28	5.05	3.33	0.73	19.2	1.0	–	7.78
Converter slag B	45.1	12.9	1.59	5.86	4.66	0.91	19.8	0.72	–	2.65
Electric furnace slag	20.7	6.83	1.78	3.54	9.63	0.24	47.5	0.21	5.88	0.08
LF slag	40.7	22.2	18.4	14.5	0.40	0.10	0.19	0.23	1.57	0.1

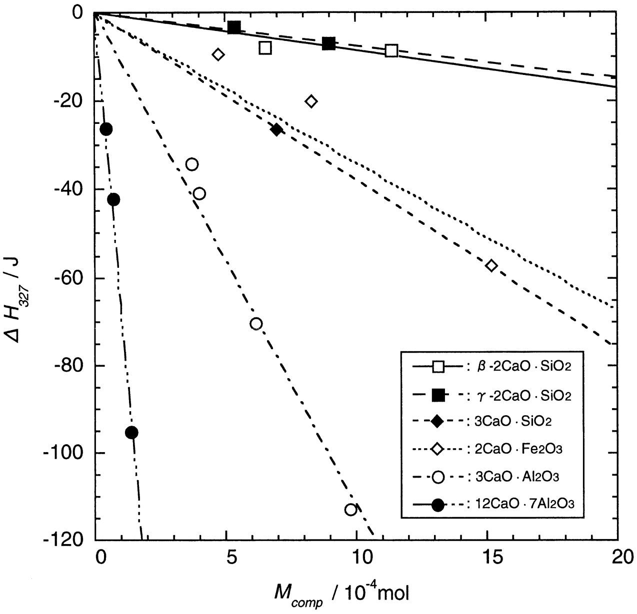

Fig. 2. Enthalpy change for hydration of CaO-based compounds in distilled water at 327 K.

relationship between M_{comp} and ΔH_{327} shown in Fig. 2. Fig. 3 demonstrates the comparison of the present and reported [16–18] ΔH_{comp} values. The value of ΔH_{comp} for $12CaO \cdot 7Al_2O_3$ was in good agreement with the reported value [18], while the values of ΔH_{comp} for $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ obtained in the present work were not agreed with those reported by Lea [16]. The unhydrated phases of $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ were detected by XRD analysis after calorimetric measurements. Two hydration stages with an induction period between the stages were reported in the hydration of calcium silicates [19]. The heat of hydration observed in the present work may correspond to that of surface hydration in the first stage for these compounds. The present values of ΔH_{comp} of $2CaO \cdot SiO_2$ agreed well with those reported by Udagawa [17] who measured the heat of initial hydration.

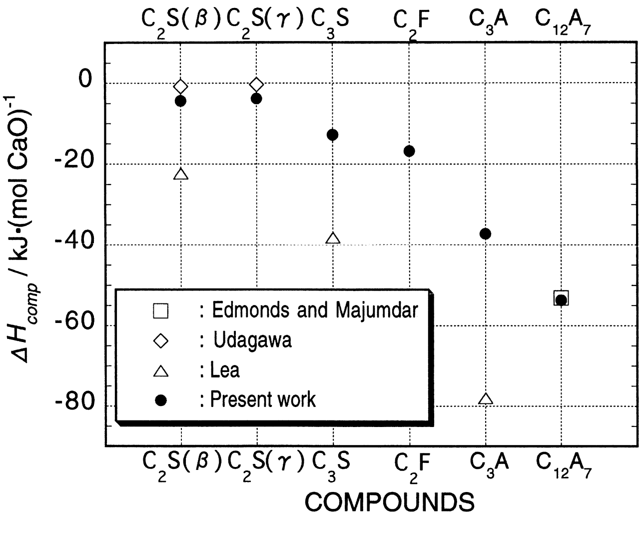

Fig. 3. Comparison of the present and reported heat of hydration of CaO-based compounds.

Fig. 4 shows volume expansion of CaO-based compounds in water at 353 K. The expansion of $3CaO \cdot Al_2O_3$ and $2CaO \cdot Fe_2O_3$ was large and not completed even after 240 h. The slow hydration rates and large volume expansion will be harmful to steam-aging treatments for stabilization of slag.

3.2. CaO solid solution

The enthalpy changes of hydration of solid solutions in CaO–FeO and CaO–MnO systems (ΔH_{327}) are shown in Fig. 5. Fig. 6 demonstrates the effect of FeO or MnO contents in the solid solutions on heat of hydration per mole of CaO (ΔH_{Sol}) which can be evaluated with the slope of lines in Fig. 5. The heat of hydration of pure lime in Fig. 6 has been reported by the present authors [20]. The values of ΔH_{Sol} of CaO–34.5mol.%MnO and CaO–44.1mol.%MnO are lower than that of pure CaO. XRD patterns of the solid solutions after hydration are shown in Fig. 7. No reflection of $Ca(OH)_2$ was found for the solid solutions with high MnO contents. The result suggests that the hydration rate decreased as MnO contents increased in higher MnO content region than 30-mol.%. Volume expansion of CaO solid solution in water of 353 K was reported [21] by Tobo et al. The relationship between the volume expansion after 240 h and ΔH_{Sol} is shown in Fig. 8. The volume expansion and heat of hydration in the lower solute content region than 30-mol.% are almost the same as those

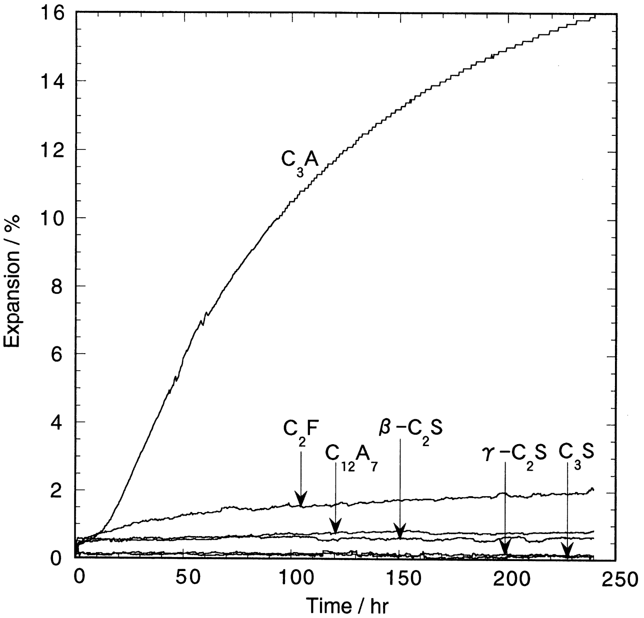

Fig. 4. Expansion curves of CaO-based compounds in water at 353 K.

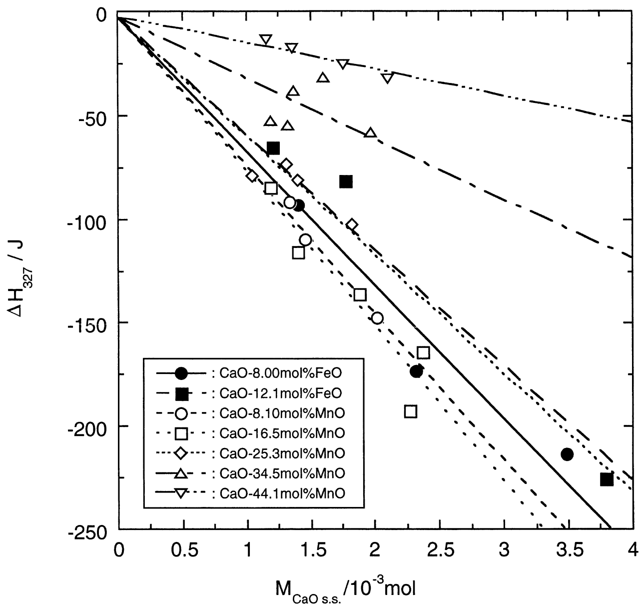

Fig. 5. Enthalpy change for hydration of CaO solid solutions in distilled water at 327 K.

of pure CaO, while volume expansion is affected by the solutes, divalent metal oxides, in the higher content region. It has been reported that divalent metal oxide contents in free lime were around 30-mol.% in high basicity slag [15], and the divalent metal oxides may be concentrated at the edge of the free lime grain [1]. Therefore, a careful steam-aging treatment is needed for high basicity steelmaking slag because of possible incorporation of divalent metal oxides in free lime.

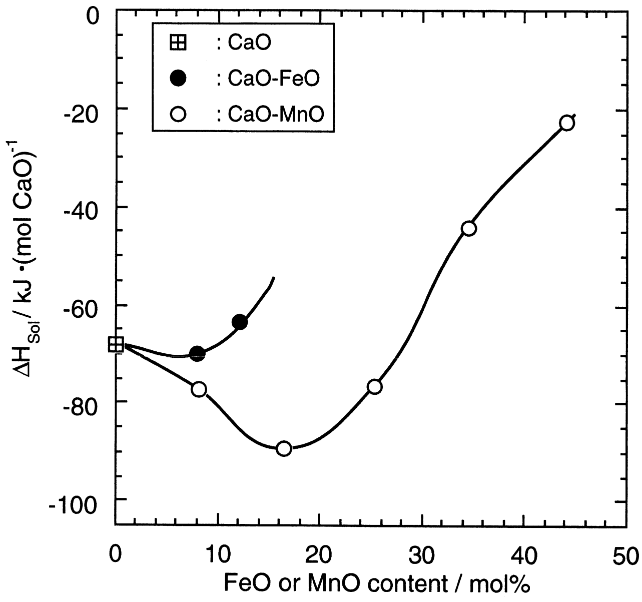

Fig. 6. Effect of FeO or MnO contents in solid solutions on heat of hydration.

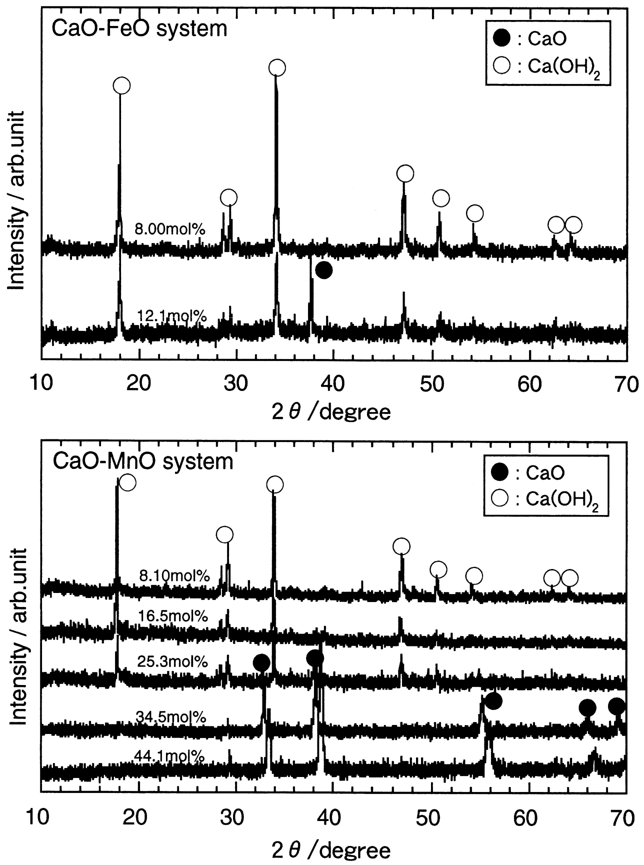

Fig. 7. XRD patterns of CaO solid solutions after hydration.

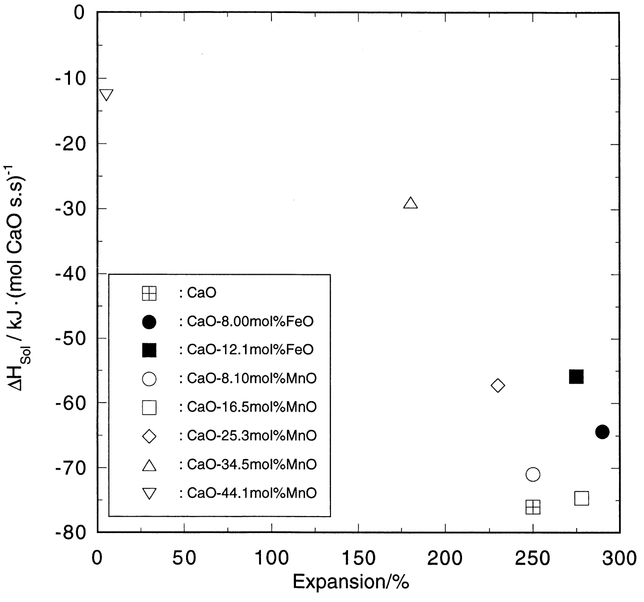

Fig. 8. Relationship between expansion and heat of hydration for CaO solid solutions.

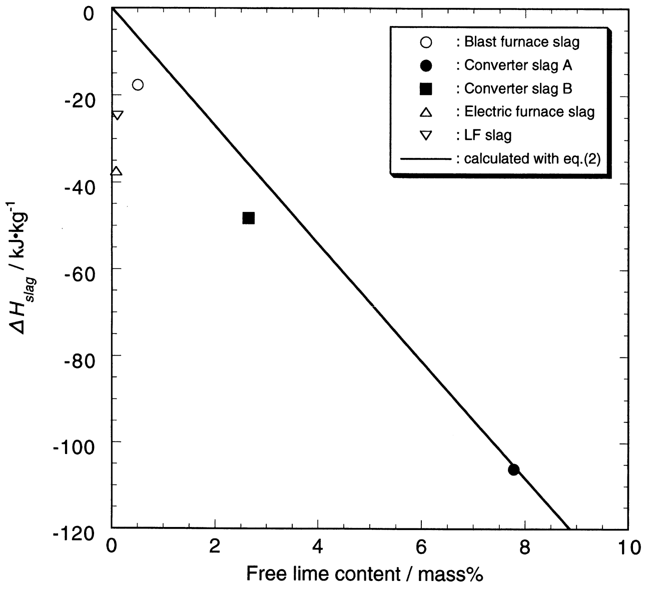

Fig. 9. Relationship between free CaO contents and heat of hydration of slags.

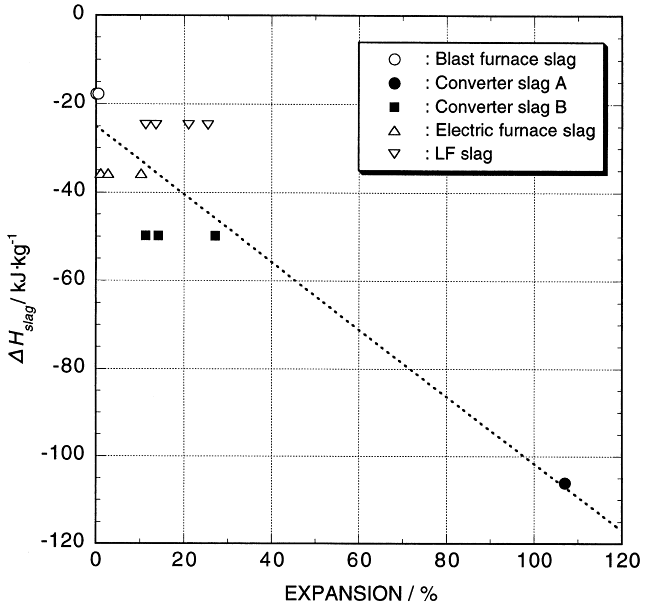

Fig. 11. Relationship between expansion and heat of hydration of slags.

3.3. Slag

Fig. 9 demonstrates the heat of hydration per kilogram of each slag (ΔH_{slag}) as a function of free lime contents. The hydration reaction of free lime in slag can be represented by Eq. (2) because the total amount of free lime in sample is within the solubility of $Ca(OH)_2$ in water at 327 K [22]

$$CaO(s) + H_2O(l) = Ca^{2+} + 2OH^{-} \tag{2}$$

The line in Fig. 9 indicates the predicted heat of hydration of slag, which is calculated with free lime contents in the slag. Fig. 10 shows volume expansion of slags. Free lime seems to dominate the hydration of converter slag and blast furnace slag because the values of ΔH_{slag} agree with those calculated and the expansion of converter slag has been completed after 50 h. On the other hand, the values of ΔH_{slag} for LF slag and electric furnace slag were higher than those calculated with free lime contents. LF slag continued volume expansion after 240 h (see Fig. 10), which means LF slag contained the component with slow expansion rates. Since an increase of Al concentration in the solvent after calorimetric measurements was detected, $3CaO \cdot Al_2O_3$ may take part in the hydration of LF slag. Fig. 11 shows the relationship between volume expansion after 240 h and ΔH_{slag}. The values of ΔH_{slag} increased with increasing of volume expansion. The volume expansion of converter slag in which free lime is a main hydration component can be evaluated by the calorimetric measurements.

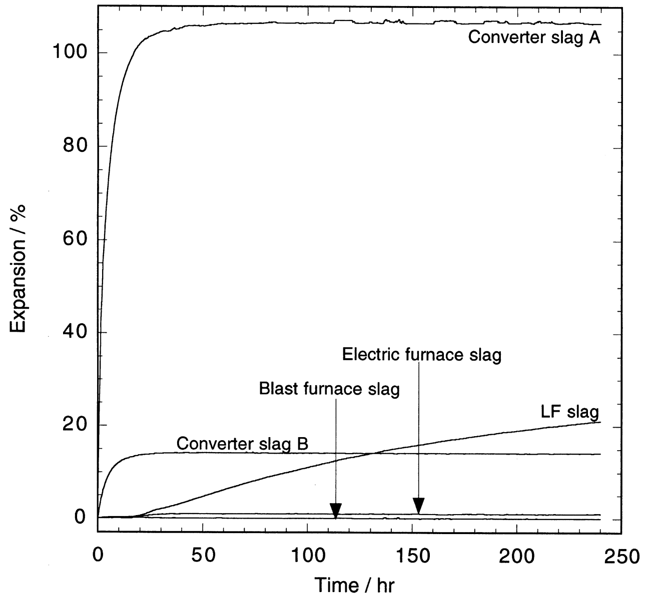

Fig. 10. Expansion curves of slags in water at 353 K.

4. Conclusions

The heat of hydration and volume expansion due to hydration were measured for CaO-based compounds, CaO solid solutions and various kind of slags as a fundamental study on disintegration of steelmaking slag, and following results were obtained.

1. The presence of $3CaO \cdot Al_2O_3$ in slag will have harmful effects on stability of the slag because of its slow hydration rate and large volume expansion.
2. Hydration behavior of CaO–FeO and CaO–MnO solid solutions was almost the same as that of pure CaO in

the lower FeO or MnO content region than 30-mol.%, while the volume expansion decreased in the higher solute content region.

3. Free lime is a main hydration component in converter slag. LF slag and electric furnace slag showed higher heat of hydration than those calculated with free lime contents, and it was suggested that $3CaO \cdot Al_2O_3$ affected the hydration of LF slag.

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