

Material Design of Cement for Increased Waste Usage and Reduction of CO₂ Emissions

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ABSTRACT

Cement industry contributes to the recycling of resources by using various industrial wastes and by-products in Japan. Furthermore, the industry must facilitate efforts to prevent global warming. Therefore, the comprehensive materials design of cement, in consideration of both environmental impacts and properties, is expected to become increasingly important. This paper describes the influence of mineral admixtures on the paste fluidity and the adiabatic temperature rising characteristic of cement containing high aluminate phase content. The fluidity of the cement paste containing aluminate phase of 12 mass% was improved by adding of mineral admixtures such as granulated blast furnace slag or limestone powder. By increasing of aluminate phase of cement and addition of mineral admixtures, it is possible to enlarge waste usage and reduce CO₂ emission without changing the performance of cement in cement industry.

INTRODUCTION

Ecocement that uses 500 kg or more of waste such as sludge per cement ton is presently manufactured in Japan. Two ecocement plants producing about 110,000 to 130,000 t/year are already in operation. The JIS for ecocement was established in 2003 [JIS R 5214]; the amount of C₃A in this cement is about 14%, a large value compared 8 to 9 % for ordinary Portland cement (OPC). On the other hand, the cement industry contributes to recycling by utilizing various industrial wastes and by-products as raw materials or fuels. However, with no hope of increasing the demand for cement in Japan, it is necessary to increase the volume of waste per unit mass in order to maintain the amount of waste consumed. In such cases, increase in heavy metals and changes in setting time by minor components such as fluorine or phosphorus become problems. Industrial waste and byproducts, such as incinerated garbage ash, sewage sludge, construction emission soil and coal ash, contain relatively large amounts of Al₂O₃. The possibility of utilizing wastes is suggested by increasing the aluminate phase content or the interstitial phase content (the total amount of aluminate phase (C₃A) and ferrite phase (C₄AF)) in the clinker [Uchikawa and Obana 1995, Oosaki 2000].

The interstitial phase of cement clinker has a higher rate of initial reaction. Hence, it is feared that an excessive increase in the interstitial phase content of cement clinker could produce concrete with lower fluidity [Spiratos et al. 2003, Sakai et al. 2003] or higher heat evolution. In this case, it will become more important to control the fluidity and the heat liberation of cement, with a growing the use of industrial wastes. A decline in fluidity causes poor concrete works, and increased heat evolution encourages thermal cracking that is harmful to reinforced concrete. It is important to grasp an adiabatic temperature rise of concrete to prevent the thermal cracking of concrete.

However, there have been few studies on the relationship between the properties, such as the fluidity or the adiabatic temperature rise, and various characteristics, such as the composition of the interstitial phase, and the amount of mineral admixtures, in cement in which the interstitial phase content exceeds that in ordinary Portland cement. In this paper, we investigated the influence of the interstitial phase composition and the addition of mineral admixtures on the fluidity and adiabatic temperature rise properties of the cement which contained a greater interstitial phase than ordinary Portland cement. In addition, this paper discusses the reduction of CO₂ emission and the usage of industrial wastes and by-products of cement with high C₃A content and mineral admixtures. And this paper proposes cement compositions for increased waste usage and the reduction of CO₂ emission.

EXPERIMENTAL INVESTIGATION

Materials

Clinker samples with different C₃A contents were prepared using special grade reagents and industrial materials including limestone, silicestone, coal ash, blast-furnace slag, and ferrous slag. These materials and reagents were mixed at specified ratios. The mixture was kneaded by adding water, and the dried mixture was molded into a cubic form. Clinkers were sintered in an electric furnace for 30 min at a maximum temperature of 1550°C, and then removed from the furnace at a temperature of 1350°C. These samples were ground using a ball mill until the Blaine specific surface area became 320±5 m²/kg.

In the investigation for the fluidity of cement, two cement samples were prepared by adding gypsum and hemihydrate to clinker and adjusting the SO₃/C₃A molar ratio to 2/3. Hemihydrate prepared by heating gypsum (special grade reagent) in the atmosphere was used. For both cements, the hemihydrate content in the total calcium sulfate content was set to 50%. Table 1 lists the mineral composition (determined by Bogue's equation) and SO₃ content in the cement samples. In the investigation of adiabatic temperature rise of cement, control sample with interstitial phase content of about 18% (determined by Bogue's equation), high C₃A samples, and high C₄AF samples were synthesized. Table 2 lists the mineral composition of the clinker samples. These samples were ground using a ball mill until the Blaine specific surface area became 320±5 m²/kg. Cement samples were prepared by adding gypsum and hemihydrate to clinker and adjusting the 2% SO₃ content.

Some samples were prepared by adding blast-furnace slag, limestone powder or fly ash. The amount of mineral admixture was changed from 10 to 20 mass%. Table 3 gives the Blaine specific surface area and the chemical composition of the mineral admixtures. A polycarboxylate was used for the superplasticizer. P-34 with graft chains of

polyethylene oxide (PEO) is α -allyl- ω -methoxypolyethylene-maleic anhydride copolymer. A small amount of styrene is incorporated within the backbone of the polymer [Sakai et al.2001].

Table 1. Mineral composition and SO₃ content in cement

Sample	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	SO ₃
Control cement	52.5	23.1	9.2	8.8	1.84
High C ₃ A cement	47.8	23.8	11.6	8.8	2.36

(mass%)

Table 2. Mineral composition of cement

Sample		Mineral composition (by Bogue's eq., mass%)				
		C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Interstitial phase
Control	A9F9	59.2	19.6	9.4	9.0	18.4
High C ₃ A	A12F9	56.6	19.4	12.1	9.1	21.2
	A15F9	57.9	15.5	15.2	8.6	23.8
High C ₄ AF	A9F12	59.7	16.5	9.1	11.8	21.0
	A9F14	58.2	15.4	9.1	14.4	23.5

Table 3. Physical and chemical properties of mineral admixtures

Sample	Symbol	Blaine (m ² /kg)	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	Unburned Carbon	Mean Diameter (μm)
Limestone Powder	LSP5000	494	55.5	0.30	0.01	0.02	-	11
	LSP9000	912	55.6	0.31	0.01	0.02	-	4
Blast-Furnace Slag	BFS	424	42.9	5.62	14.8	0.30	-	12
Fly Ash	FA	340	3.0	0.75	29.7	6.25	2.86	20

Measurement of fluidity of paste

To prepare the paste, the water-cement ratio (W/C) was fixed at 0.32 by mass. The dosage of superplasticizer was 0.048 mass% (as determined by the ratio of solid polymer content to cement). De-ionized water, in which the superplasticizer had been initially dissolved, was added to the cement, and a paste was prepared in a thermostatic chamber set to 20°C. The paste was prepared using a hand mixer for a mixing time of 10 min. After mixing, the fluidity of the paste was evaluated using a concentric-cylinder rotational viscometer (Rotovisco RT20 made by Haake, Inc.; radius of the inner cylinder, 20.71 mm; clearance between the inner and outer cylinders, 0.99 mm; with smooth surface). The time from filling to measurement was minimized to minimize the effect of segregation. The shear stress was increased from 0 to 200 Pa over 3 min, and the apparent viscosity was then measured at 200 Pa.

Evaluation of initial heat of hydration

The C_3A of cement reacts rapidly with water. Hence, the measurement of the initial heat liberation of high C_3A cement requires special equipment that has a higher response speed than a conventional conduction calorimeter. Furthermore, such cement paste with low W/C is difficult to mix in an apparatus. Thus, we modified existing equipment (isothermal calorimeter; IC-20 made by Tokyo Riko Corp. Ltd.) by changing the temperature sensor from a thermo module to a thermocouple and by converting the inner agitating blade from a propeller type to a comb type (Fig. 1). We used this equipment to compare the very early reaction rate of the cement sample [Maruya et al.



Fig. 1. Description of prototype equipment [Maruya et al. 2009].

Measurement of temperature rise of mortar

The adiabatic temperature rise of mortar containing with different C_3A contents was measured by small sample adiabatic calorimeter (Tokyo Riko Corp. Ltd.). This equipment uses a 30 ml sample in a film case, which is used as a sample container [Maruya et al. 2009]. The adiabatic state can be controlled by adjustment of the temperature of surrounding air to follow that of sample. The fewer the samples, the harder it is to maintain exact adiabatic control. The measurement time was set over 3 days in such a way that the temperature rise becomes moderate. The water-cement ratio (W/C) and sand-cement ratio (S/C) of mortar was fixed at 0.5 and 2.5, respectively. The mortar was prepared by hand mixing because the volume of samples was small. After mixing the cement and water with a mixing time of 2 min, sand was added into the mixture and then stirred for 3 min. The mortar was prepared in a thermostatic chamber set to $20 \pm 1^\circ\text{C}$. After mixing, the mortar sample was set into the sample container, and then thermocouples were inserted for measuring and controlling the temperature. Silicon grease was applied around the insertion site to prevent water dissipation.

Mortar test

Compressive strength and length change of mortar was measured by JIS R 5201 and JIS A 1129-1, respectively.

RESULTS AND DISCUSSION

Adiabatic temperature rise of mortar

For the mortar sample of high C_3A cements and high C_4AF cements prepared with $S/C=2.5$, the adiabatic temperature rise curves are shown in Fig.2. The change in the adiabatic temperature rise with increasing of the interstitial phase content differed between high C_3A cements and high C_4AF cements. When the C_3A content was increased, the temperature rise of samples was equal to that of control sample until 0.6 day. However, since then, the temperature rise increased depending on the C_3A content. Especially with the sample containing C_3A of 15 mass%, the temperature rise in the period of one day reached the same level with control sample obtained in the period of three days, and ultimate temperature rise appeared rapidly. In contrast, when the C_4AF content was increased, the temperature rise of samples after 0.6 day increased with increasing of C_4AF content, but the differences between samples were small. It was confirmed that changes in adiabatic temperature rise were negligible even when the C_3A content of cement was increased from 9 mass% to 12 mass%, or the C_4AF content of cement was increased from 9 mass% to 14 mass%. Fig.3 shows the effect of blast-furnace slag on the adiabatic temperature rise for cements with different interstitial composition. For the control sample with interstitial phase content of 18 mass%, the ultimate adiabatic temperature rise of mortar slightly increased by adding blast-furnace slag. However, in case of samples containing large amount of C_3A , the temperature rise of mortar was decreased by adding blast-furnace slag of 20 mass%. The blast-furnace slag showed a beneficial effect upon the heat liberation of cement with increased interstitial phase content.

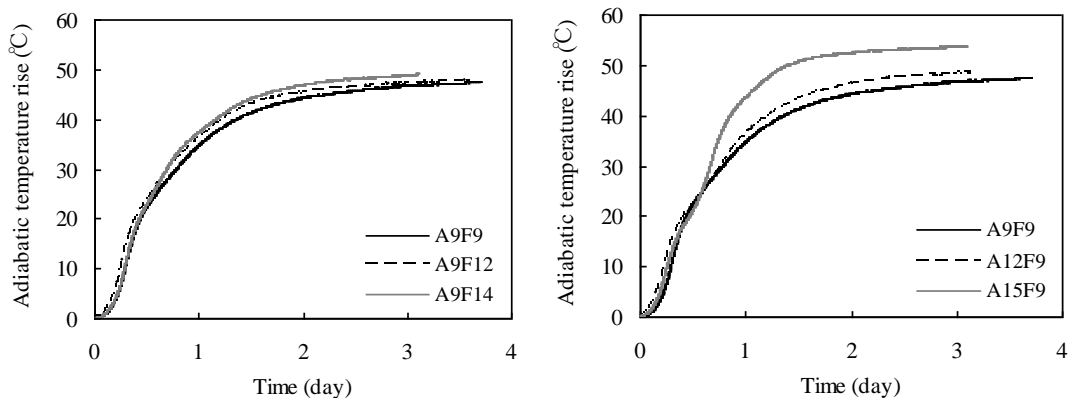


Fig.2. Influence of C_3A or C_4AF contents on adiabatic temperature rise of mortars

Effect of the Mineral Admixture on Paste Fluidity

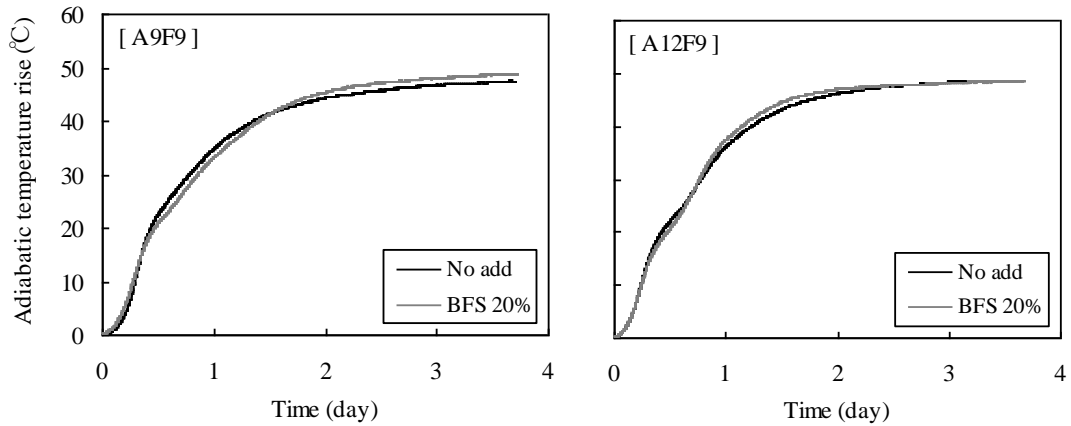


Fig.3. Influence of blast furnace slag on adiabatic temperature rise of mortar

The apparent viscosity of the paste for cements with or without mineral admixture is shown in Fig. 4. For the high C_3A sample, the apparent viscosity of the paste was decreased by adding blast-furnace slag or limestone powder of 10 mass%. When the limestone powder was added, the apparent viscosity of the paste was less than that of the control sample (C_3A 9%, without mineral admixture), regardless of the fineness of the limestone powder.

The fluidity of cement paste with high C_3A content was improved by adding of blast furnace slag more than 20 mass%. This is the dilution effect of C_3A by adding of mineral admixture. The fluidity of cement paste is generally expected to improve with the addition of mineral admixture because of the dilution effect. However, the vast improvement by limestone powder could not be explained as resulting from only the dilution of C_3A .

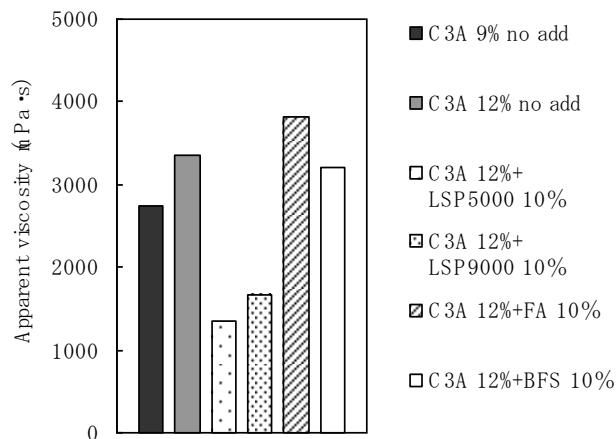


Fig. 4. Influence of mineral admixture on the paste fluidity (with 0.048% superplasticizer)

Relationship between Initial Heat Liberation and Paste Fluidity

When the mineral admixture was not added, the rate of heat liberation of high C₃A cement exceeded that of the control sample as expected. When limestone powder of 10 mass% was added, the rate of heat liberation decreased below that of the control sample, as did the apparent viscosity. These results indicate that the very early hydration of high C₃A cement is inhibited by adding limestone powder, and the amount of hydrates is significantly decreased. Limestone powder is known to inhibit the hydration of C₃A because it forms gel-like hydrates containing carbonate ions and the hydrates act as a dense layer on the surface of C₃A [Daimon and Sakai 1998]. Similarly, the very early hydration of high C₃A cement in this test could have been efficiently inhibited by carbonate ions derived from limestone powder.

The relationship between the maximum rate of heat liberation of paste and the apparent viscosity of the paste is depicted in Fig. 5. The apparent viscosity of the paste tended to decrease with a decrease of the maximum rate of heat liberation of paste, and they were well correlated. It would appear that the high C₃A cement rapidly produced hydrates in the very early stage of hydration, so the superplasticizer adsorbed on the surface of cement was incorporated into the hydrates. When limestone powder is added, such action is impaired, and good fluidity could be obtained with less absorption of superplasticizer. There is also more superplasticizer per unit mass of clinker so dispersion will be better assuming it is more important to disperse cement than limestone.

CO₂ emission and usage of waste in high C₃A cement with mineral admixtures

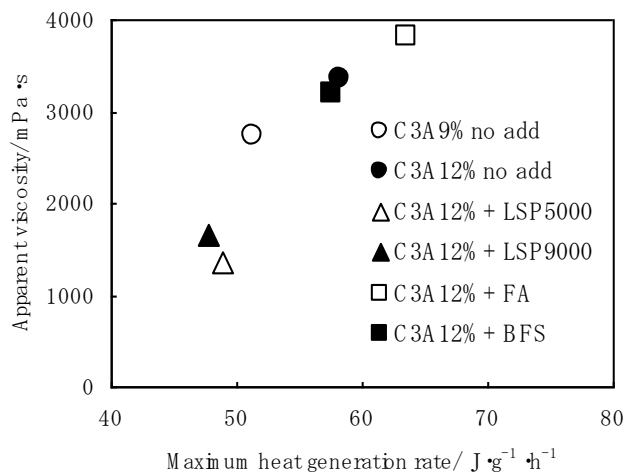


Fig. 5. Relationship between the maximum rate of heat liberation and the apparent viscosity of paste (with 0.048% superplasticizer)

By adding of mineral admixtures, the fluidity and the adiabatic temperature rise of cement with 12% C₃A is as same as that of cement with 9% C₃A which is commercial ordinary Portland cement in Japan. For the improvement of fluidity of cement with 12% C₃A, it is necessary that the dosage of blast furnace slag is over 20 mass% and that of limestone powder is over 10 mass%. Table 4 shows the CO₂ emission and the waste usage in cement with different C₃A content. For example, the symbol <A9F9> represents 9% C₃A and 9% C₄AF content in mineral composition of cement. These values were calculated based on the data and raw materials of actual cement plant. By adding of mineral admixtures, the CO₂ emission is reduced with replacement ratio of mineral admixtures. Waste usage of cement production can be increased by increasing of interstitial phase (C₃A and C₄AF content). For example, in the case of A12F11 (C₃A 12%, C₄AF 11%) and the additional of mineral admixture, waste usage is 1.12 to 1.4 times of A9F9 that is commercial product in Japan.

Compressive strength and length change of mortar are shown in Table 5. For compressive strength, A12F11 and A12A9 cement with mineral admixtures meet in 42.5

Table 4 . Waste usage and the reduction of CO₂ emission of cement

Symbol	Interstitial phase (%)		Dosage of mineral admixture (Reduction of CO ₂ : %)	Waste usage (kg/t)
	C ₃ A	C ₄ AF		
A9F9	9	9	–	256
A9F12	9	12	0	298
			10	268
			20	238
A12F9	12	9	0	329
			10	296
			20	263
A12F11	12	11	0	359
			10	323
			20	287
A12F12	12	12	0	373
			10	336
			20	298

(A9F9:Average mineral composition of commercial OPC in Japan)

Waste: Blast furnace slag, coal ash, sludge construction emission soil and bunt residue

class cement of ISO. Length change of mortar with A12F11 cement is slightly increased by adding of blast furnace slag cement. But, there are small different in length change of mortar with high C₃A content cement and mineral admixtures compared with that of A9F9. By using these cements, the reduction of CO₂ emission and the increase of waste usage can be realized. These cements are available as soft environmental cement. But, the standard of cement in Japan is different from ISO, and we have no standard for strength class type of cement. More detail investigations containing the investigation for standard of cement are necessary for practical use of these cements.

CONCLUSIONS

This study investigated the influence of the interstitial phase composition and the addition

Table 5. Properties of mortar containing cement with high C₃A content and mineral admixtures

Cement	Mineral admixture	Compressive strength (N/mm ²)	Length change (10 ⁻⁶) 112d
A9F9	0	52.3	-729
A12F9	BFS 20%	50.3	-793
A12F11	BFS 20%	45.8	-807
A12F11	LSP 20%	42.9	-657

of mineral admixtures on the fluidity and adiabatic temperature rise properties of the cement which contained a greater interstitial phase than ordinary Portland cement. And this paper discusses the reduction of CO₂ emission and the usage of industrial wastes and by-products of cement with high C₃A content and mineral admixtures.

Changes in adiabatic temperature rise were negligible even when the C₃A content of cement was increased from 9 mass% to 12 mass%, or the C₄AF content of cement was increased from 9 mass% to 14 mass%. In case of samples containing large amount of C₃A or C₄AF, the adiabatic temperature rise of mortar was decreased by adding blast-furnace slag of 20 mass%.

By adding of mineral admixtures such as blast furnace slag and limestone powder, the fluidity of cement with high C₃A content can be improved. Limestone powder exhibited much more improvement in fluidity than blast-furnace slag and fly ash. For the heat liberation in the very early stage of hydration, the hydration of cement was found to be inhibited by the addition of limestone powder using equipment modified to respond to thermal change more rapidly than a conventional conduction calorimeter. The rate of very early heat liberation was highly correlated with the apparent viscosity of paste containing superplasticizer. This result indicates that adding limestone powder could be an effective way to control the fluidity of cement with increased C₃A content.

By using cements containing 12% C₃A and 9-12% C₄AF contents and mineral admixtures such as blast furnace slag and limestone powder, it is possible to enlarge waste usage and reduce CO₂ emission without changing the performance of cement in cement industry.

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