Characteristics for Improvement of Compressive Strength of Geopolymers Made of Mixed Binders

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Abstract: Geopolymers are composite hard materials made by mixing binders, such as fly ash and slags, and activators, such as NaOH and sodium silicate. The chemical mechanism for hardening composite materials, aluminosilicate binders, with alkaline activators is known as a geopolymer reaction. Geopolymers have recently been developed to be used as a replacement for Portland cement concrete. Industrial by-products such as fly ash, steel making slags, and garbage melting furnace slags can be made into geopolymers in a process that emits less carbon dioxide than in the cement making process. This reduction in CO_2 emission is important because CO_2 is one of the substances known to contribute to global warming. In the future, further uses of these fly ash and slags must be explored. The development of high compressive strength geopolymers using fly ash and slags will strongly contribute to the fields of construction, geotechnical engineering, and architecture.

So far, ground blast furnace slag has yielded the highest compressive strength geopolymer among various kind of binders such as fly ash, ground stainless steel-making slag, and garbage melting furnace slags. A potential use for the poor binders, yielding low compressive strength geopolymers, is to combine it with a richer binder to create stronger products. This paper examines the characteristics for improvement of compressive strength of geopolymers for the binders in various mixture ratios of poor binders and the ground blast furnace slag.

Keywords: Binder, Chemical composition*,* Compressive strength, Geopolymer, Strength Improvement characteristic.

1. INTRODUCTION

More than 60 million ton of industrial by-products such as fly ash, steel slags and garbage melting furnace slags are generated every year in Japan [1]. Geopolymers are composite hard materials made by mixing binders, such as fly ash and slags, and activators, such as NaOH and sodium silicate [2]. The chemical mechanism for hardening composite materials, aluminosilicate binders, with alkaline activators is known as a geopolymer reaction [3]. Geopolymers have recently been developed to be used as a replacement for Portland cement concrete. Industrial by-products such as fly ash, steel making slags, and garbage melting furnace slags can be used to create geopolymers in a process that emits less carbon dioxide than in the cement making process. This reduction in CO_2 emission is important because CO_2 is one of the substances known to contribute to global warming. In the future, further uses of these fly ash and slags must be explored. The development of high compressive strength geopolymer using fly ash and slags will strongly contribute to the fields of construction, geotechnical engineering, and architecture.

Koumoto [1] has found the ground blast furnace slag to be the binder that yielded the highest compressive strength geopolymer among various kind of binders such as fly ash, ground stainless steel-making slag, and garbage melting furnace slags. Poor binders, yielding low compressive strength geopolymers can be effectively strengthened by combining with a richer binder, such as ground blast furnace slags. In this research the characteristics for improvement of compressive strength of geopolymers for binders in various mixture ratios of poor binders and the ground blast furnace slag are examined.

2. MATERIALS

2.1. Preparation of Binders

To examine the characteristics for improvement of compressive strength of geopolymer made of mixed binders, four cases of mixed binders: a. Reihoku+Koro, b. Karita+Koro, c. Stainless+Koro and d. Kazusa+Koro were prepared. Reihoku and Karita are fly ash, Stainless is ground stainless steel-making slag, Kazusa is garbage melting furnace, and Koro is ground blast furnace slag. In each case binders were mixed in various mixture ratio of δ which is defined by the following equation as:

$$\delta = b2 / (b1+b2) \quad (1)$$

where b1: binder1 and b2: binder2.

The main chemical compositions of the mixed binders tested are listed in Table **1**. In Table **1**,

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Table 1: Chemical Compositions of Tested Binders

Binders	Name of samples	Mixture ratio	Chemical composition (%)					
		δ= =b2/(b1+b2)	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3
Reihoku+Koro b1=Reihoku b2=Koro	Reihoku*	0.00	55.0	21.1	9.1	5.3	1.1	0.9
	KoroRei5	0.17	51.6	20.1	14.7	4.5	1.9	0.8
	ReiKoro*	0.50	44.8	18.0	25.9	2.9	3.4	0.5
	ReiKoro2*	0.67	41.4	16.9	31.5	2.0	4.2	0.3
Karita+Koro b1=Karita b2=Koro	Karita*	0.00	38.8	24.3	19.5	1.5	0.5	6.6
	KoroKari5	0.17	38.1	22.7	23.4	1.4	1.4	5.5
	KariKoro*	0.50	36.7	19.5	31.1	1.0	3.1	3.3
	KariKoro2*	0.67	36.0	18.0	35.0	0.8	4.0	2.2
	KariKoro5	0.83	35.3	16.4	38.8	0.6	4.8	1.1
Stainless+Koro b1=Stainless b2=Koro	Stainless*	0.00	26.7	5.3	48.2	1.0	5.5	0.4
	KoroSta5	0.17	28.0	6.9	47.3	0.9	5.5	0.3
	KoroSta2	0.33	29.4	8.5	46.3	0.8	5.5	0.3
	StaKoro	0.50	30.7	10.1	45.4	0.7	5.6	0.2
	StaKoro2	0.67	32.0	11.6	44.5	0.8	5.6	0.1
Kazusa+Koro b1=Kazusa b2=Koro	Kazusa*	0.00	34.2	13.2	42.0	2.6	1.9	0.7
	KoroKazu3	0.25	34.3	13.7	42.2	1.9	3.2	0.5
	KazuKoro*	0.50	34.4	14.0	42.4	1.5	3.8	0.4
	KazuKoro2*	0.67	34.5	14.3	42.5	1.1	4.4	0.2
	KazuKoro5	0.83	34.5	14.5	42.6	0.8	5.1	0.1
b1=0, b2=Koro	Koro*	1.00	34.6	14.8	42.7	0.4	5.7	0.0

Note: Reihoku and Karaita= Fly ash; Koro= ground blast furnace slag; Stainless= ground stainless steel-making slag; Kazusa= ground garbage melting furnace slag.
*: data from Koumoto [1].

Reihoku, Karita, Stainless, and Kazusa = binder1 (poor binder) and Koro = binder2 (richer binder).

Figure **1** shows a triangular coordinate display for chemical compositions of binders listed in Table **1**. In Figure **1a** triangle is drawn for CaO, SiO_2 and Al_2O_3+others. This display method helps us to understand the situation of chemical compositions of mixed binders according to the mixture.

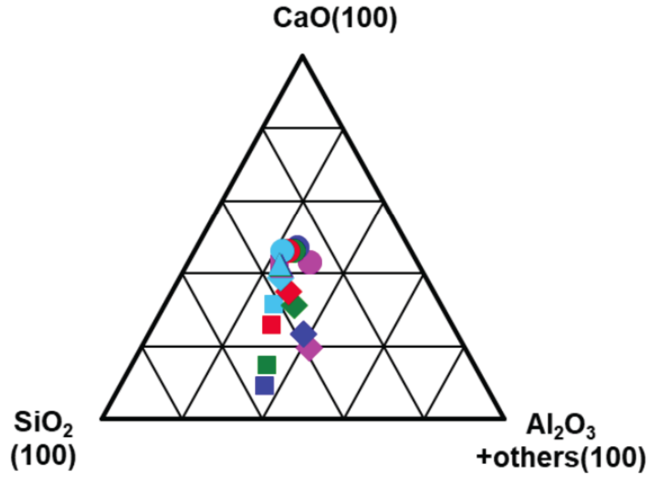
2.2. Making of Geopolymer Samples

Although there are several kinds of liquid sodium hydroxide and sodium silicate as activators, in this research both 48%NaOH (18 mol/L) and Sodium silicate ($Na_2 . nSiO_2$, n = 3.2) which are commercial and expected to yield the high compressive strength geopolymers because of their high concentration, are used. The compressive strengths of geopolymers q_u is generally considered as a function of w (= weight ratio of activator to binder) and η (= weight ratio of NaOH to Sodium silicate). In this research, according to Koumoto [1], the w_{opt}, which is the optimum value of w yielding the ultimate compressive strength q_{umax}, becomes a constant value of w = 0.4. Geopolymer samples were made for variable η value with a value of w = 0.4. The geopolymer samples were filled up after mixing the activator and binder in the plastic molds of diameter φ = 50mm×height h = 100mm with slight vibration. The geopolymer samples were removed from the mold after one or two days and cured at room temperature under the dried condition for 28 days.

3. TEST AND RESULTS

3.1. Compression Tests

Before compression test, physical properties of geopolymer samples such as diameter (d), height (h), and weight (W) were measured to obtain characteristics of shrinkage and density. Compression tests of geopolymer samples were carried out at the Saga Construction Technology Support Organization (SCTSO) using the concrete testing apparatus in the



CaO	SiO2	marker	sample
42.7	34.6	■	Koro
9.1	55.0	■	Reihoku
14.7	51.6	■	KoroRei5
25.9	44.8	■	ReiKoro
31.5	41.4	■	ReiKoro2
19.5	38.8	◆	Karita
23.4	38.1	◆	KoroKari5
31.1	36.7	◆	KariKoro
35.0	36.0	◆	KariKoro2
38.8	36.3	◆	KariKoro5
43.2	26.7	●	Stainless
47.3	28.0	●	KoroSta5
46.3	29.4	●	KoroSta2
46.4	30.7	●	StaKoro
46.5	32.0	●	StaKoro2
42.0	34.2	▲	Kazusa
42.2	34.3	▲	KoroKazu3
42.4	34.4	▲	KazuKoro
42.5	34.5	▲	KazuKoro2
42.6	34.5	▲	KazuKoro5

Figure 1: Triangular coordinate display for chemical compositions of binders of geopolymer samples.

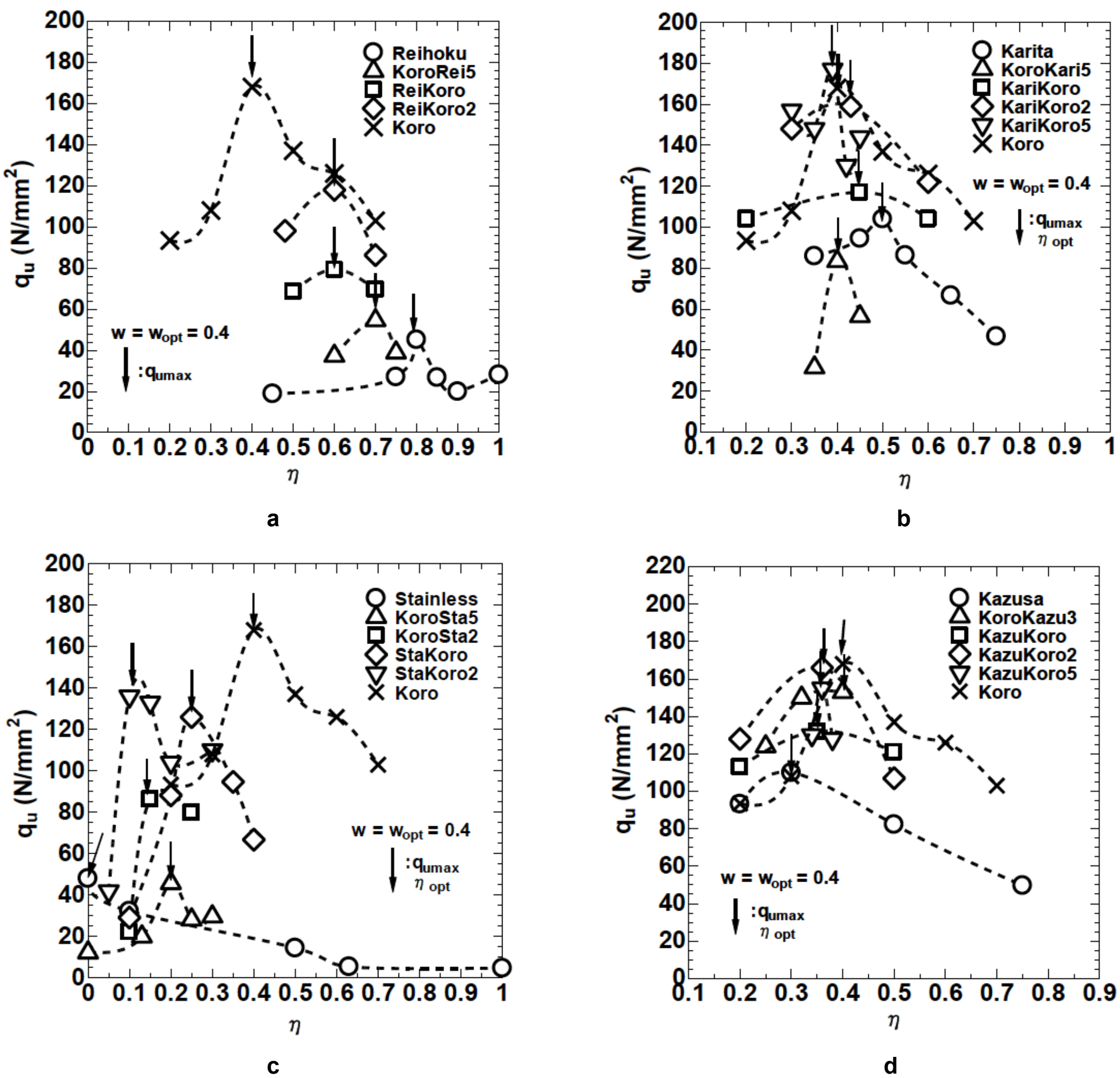


Figure 2: Compression test results for geopolymers: (**a**) Reihoku+Koro; (**b**) Karita+Koro; (**c**) Stainless+Koro; (**d**) Kazusa+Koro.

Table 2: Compression Test Results of Geopolymer Samples

Binders	Name of samples	Mixture ratio	Compression test results				
		δ=b2/(b1+b2)	q_{umax} (N/mm^2)	w_{opt}	η_{opt}	ρ_t (kg/m^3)	ΔV/V(%)
Reihoku+Koro b1=Reihoku b2=Koro	Reihoku*	0.00	45.2	0.40	0.80	1,868	0.20
	KoroRei5	0.17	54.6	0.40	0.70	2,016	1.99
	ReiKoro*	0.50	79.3	0.40	0.60	2,098	0.70
	ReiKoro2*	0.67	118.0	0.40	0.60	2,144	1.20
Karita+Koro b1=Karita b2=Koro	Karita*	0.00	104.3	0.40	0.50	1,985	0.20
	KoroKari5	0.17	83.4	0.40	0.40	2,144	0.50
	KariKoro*	0.50	117.0	0.40	0.45	2,122	0.90
	KariKoro2*	0.67	159.0	0.40	0.43	2,149	0.70
	KariKoro5	0.83	177.0	0.40	0.39	2,183	1.09
Stainless+Koro b1=Stainless b2=Koro	Stainless*	0.00	48.1	0.40	0.00	2,269	11.34
	KoroSta5	0.17	45.8	0.40	0.20	2,367	5.69
	KoroSta2	0.33	86.6	0.40	0.20	2,296	6.17
	StaKoro	0.50	126.0	0.40	0.25	2,243	3.26
	StaKoro2	0.67	136.0	0.40	0.10	2,261	2.68
Kazusa+Koro b1=Kazusa b2=Koro	Kazusa*	0.00	110.0	0.40	0.30	2,202	1.49
	KoroKazu3	0.25	153.0	0.40	0.40	2,183	2.08
	KazuKoro*	0.50	132.0	0.40	0.35	2,219	1.29
	KazuKoro2*	0.67	166.0	0.40	0.36	2,218	1.49
	KazuKoro5	0.83	155.0	0.40	0.36	2,349	1.49
b1=0, b2=Koro	Koro*	1.00	168.0	0.40	0.40	2,227	1.20

Note: q_{umax}= maximum value of compressive strength q_u; w_{opt}= optimum value of w yielding q_{umax}; η_{opt}= optimum value of η yielding q_{umax}; ρ_t= density of geopolymer sample yielded qumax; ΔV/V= volume shrinkage ratio of geopolymer sample yielded qumax.
*: data from Koumoto [1].

same test method for concrete samples (sample diameter d = 50mm and height h = 100mm, loading rate = 0.6 ± 0.4 N/mm^2 and loading plate φ = 300 mm).

3.2. Test Results

Compression test results are shown in Figure **2a**, **b**, **c** and **d** which show the relationship between the compressive strength q_u and η for w = w_{opt} = 0.4. As shown in Figure **2a**, **b**, **c** and **d**, q_u generally increases with an increase in η and reach the maximum value q_{umax} at a certain η value, which is defined as the optimum value η_{opt}. The values of q_{umax} and η_{opt} from Figure **2a**, **b**, **c** and **d** are summarized in Table **2**. Table **2** also includes the value of w_{opt} and both values of the density ρ_t and the volume shrinkage ratio ΔV/V of geopolymer sample yielded the q_{umax}.

4. DISCUSSIONS

4.1. Relationship between q_{umax} and Mixture Ratio of Binders δ

Figure **3a**, **b**, **c** and **d** shows the relationship between q_{umax} and δ. From Figure **3a**, **b**, **c** and **d** the q_{umax} generally increases with an increase of δ along the broken straight line which is drawn between the q_{umax} for binder1 and the one for binder2 (Koro). It is interesting that in the case of Figure **3c** Karita+Koro, the value of q_{umax} for δ = 0.83 becomes larger than that for δ = 1 (Koro).

Figure **4** shows the relationship between q_{umax} and C_{cas} (= $CaO/(Al_2O_3 + SiO_2)$). From Figure **4** the q_{umax} increases with an increase of the factor C_{cas} until C_{cas} becomes 0.75, after that q_{umax} decreases with an increase of C_{cas}. The relationship of q_{umax} and C_{cas} seems to become a curve showing a peak at C_{cas} of 0.75.

4.2. Relationship between η_{opt} and δ

Figure **5** shows the relationship between η_{opt} and δ. From Figure **5** the η_{opt} for each binder1 (δ = 0) approaches to the η_{opt} for Koro (δ = 1) with an increase of δ.

Figure **6** shows correlation between η_{opt} and C_{cas}. The relationship between η_{opt} and C_{cas} is expressed by the following equation with a high correlation coefficient of r=0.932 as

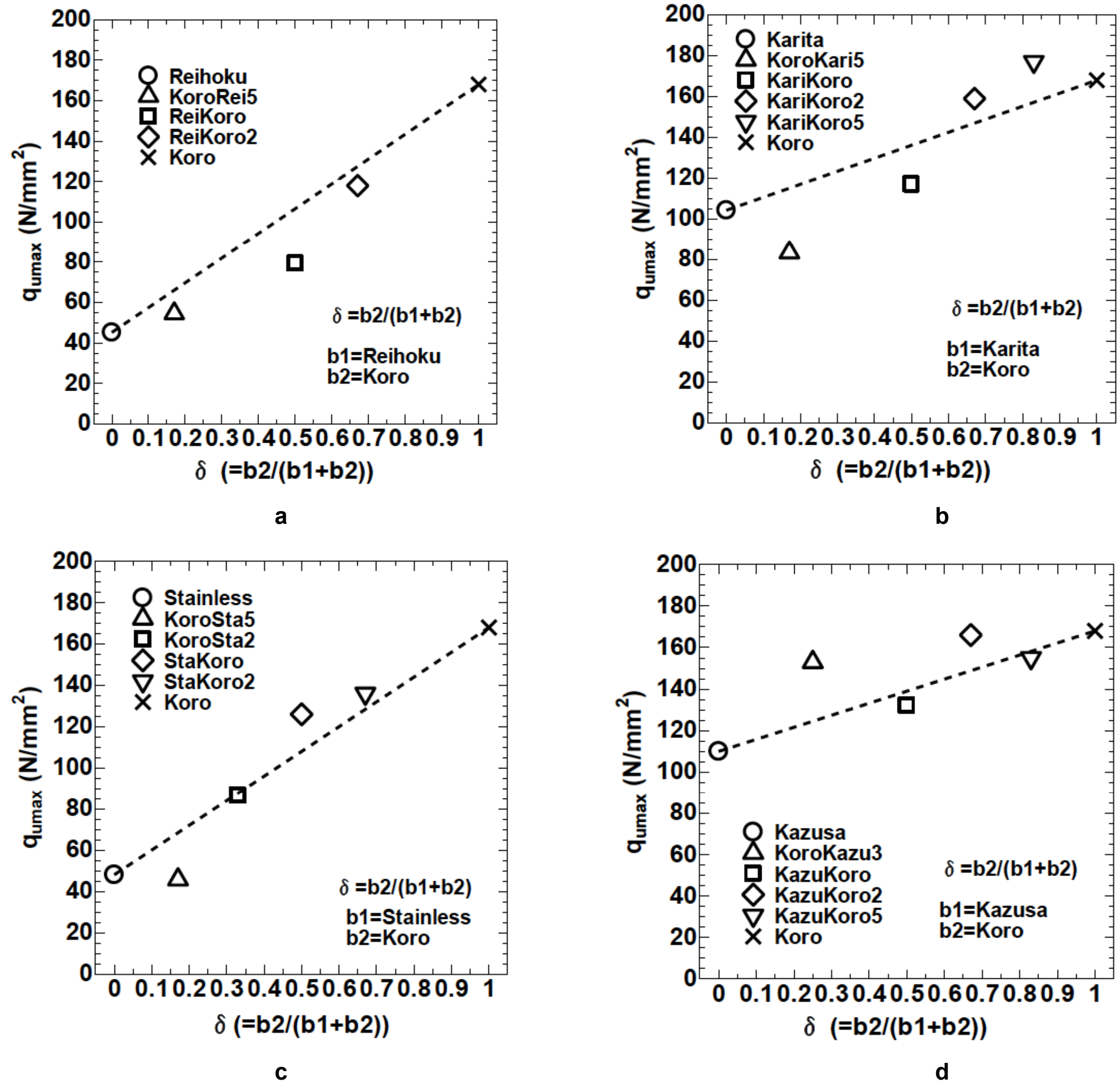


Figure 3: Relationship between q_{umax} and δ: (**a**) Reihoku+Koro; (**b**) Karita+Koro; (**c**) Stainless+Koro; (**d**) Kazusa+Koro.

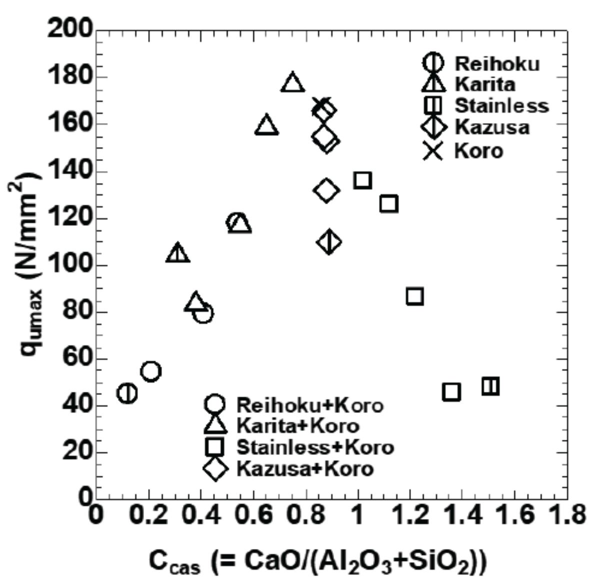


Figure 4: Relationship between q_{umax} and C_{cas}.

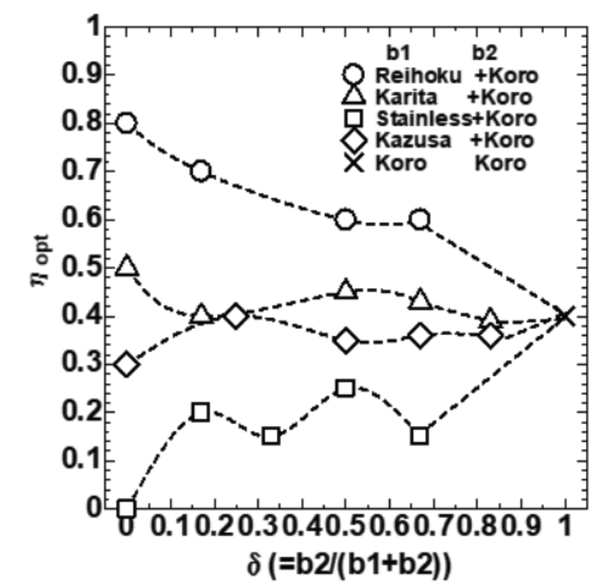


Figure 5: Relationship between η_{opt} and δ.

$$\eta_{opt} = 0.842 - 0.580 C_{cas}^{0.855} \quad (2)$$

Eq. (2) is used to calculate the η_{opt} value from the value of C_{cas} (= $CaO/(Al_2O_3+SiO_2)$) of binders to effectively produce high compressive strength geopolymers.

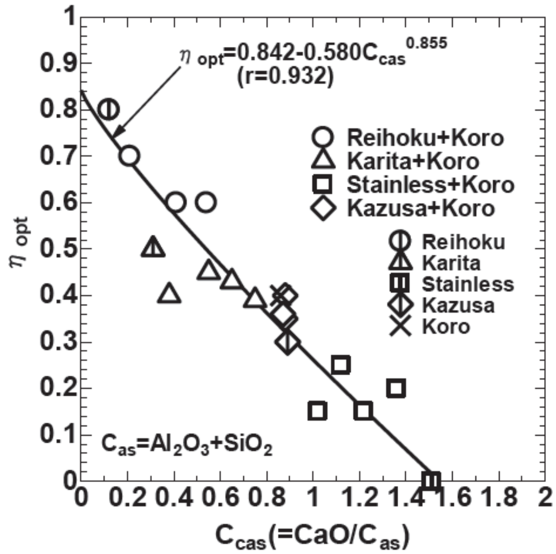


Figure 6: Correlation between η_{opt} and C_{cas}.

4.3. Relationship between ΔV/V and δ

Figure **7** shows the relationship between the volume shrinkage ratio for geopolymer sample yielded q_{umax} ΔV/V and δ. In Figure **7** the ΔV/V in the case of binder1 Stainless is the largest among all binder1 (Reihoku, Karita, Stainless and Kazusa) and the ΔV/V in the cases of other binder1 are rather lower than ΔV/V = 2 %. From Figure **7** the ΔV/V of Stainless is remarkably improved with an increase of δ.

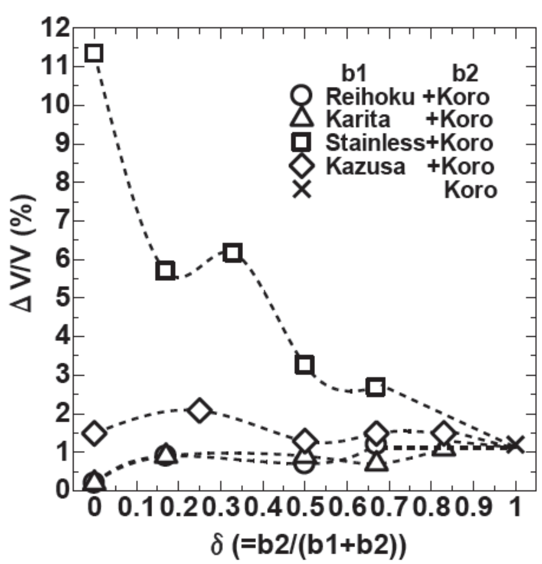


Figure 7: Relationship between ΔV/V and δ.

Figure **8** shows the relationship between ΔV/V and C_{cas}. From Figure **8** generally the smaller the C_{cas} of the binder1 the smaller the ΔV/V of the geopolymer. It is said that mixing the stainless (binder1) with the Koro (binder2) remarkably improves the ΔV/V of the geopolymer of the Stainless.

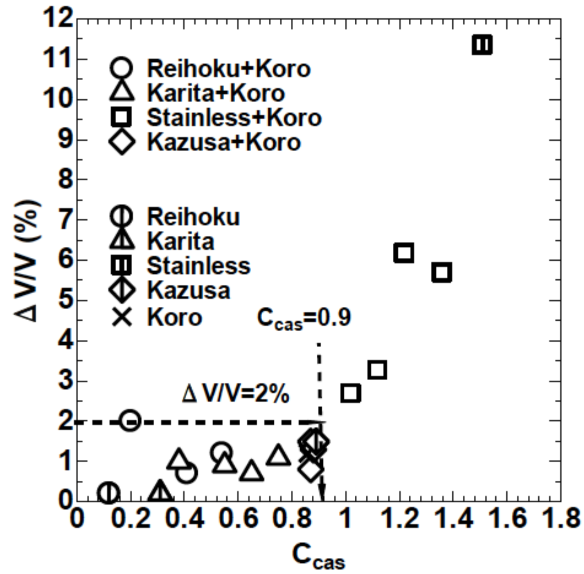


Figure 8: Relationship between ΔV/V and C_{cas}.

5. CONCLUSIONS

In the research, the characteristics for improvement of compressive strength of geopolymers for the binders in various mixture ratios of poor binders and the ground blast furnace slag (Koro) are examined.

The research results are summarized as:

1. Triangular coordinate display method in which a triangle is drawn for CaO, SiO_2 and Al_2O_3+others help us to understand the situation of chemical compositions of mixed binders according to the mixture.

2. The q_{umax} generally increases with an increase of δ along the broken straight line which is drawn between the q_{umax} for binder1 and the one for binder2 (Koro).

3. The η_{opt} for each binder1 (δ = 0) approaches to the η_{opt} for Koro (δ = 1) with an increase of δ.

4. The correlation between η_{opt} and C_{cas} (=$CaO/(Al_2O_3 + SiO_2)$) is expressed by the following equation with a high correlation coefficient of r=0.932 as:

$\eta_{opt} = 0.842 - 0.580C_{cas}^{0.855}$ in which $C_{cas} = CaO/(Al_2O_3 + SiO_2)$.

This equation is used to calculate the η_{opt} value from the value of C_{cas} of binders to effectively produce high compressive strength geopolymers.

5. In the case of binder1, Stainless is the largest ΔV/V among all binder1 (Reihoku, Karita, Stainless and Kazusa) and the ΔV/V in the cases of other binder1 are lower than ΔV/V = 2 %.

In the case of Stainless the ΔV/V can be remarkably improved from 11 % until 2 % by mixing with the binder of Koro.

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