ORIGINAL ARTICLE



Evaluating the strength development of mortar using clinker fine aggregate with a combination of fly ash and its inhibitory effects on alkali–silica reaction and delayed ettringite formation

Shintaro Miyamoto¹ · Daiki Naruse¹ · Kensuke Hayashi² · Hiroshi Minagawa¹ · Makoto Hisada¹

Received: 23 May 2022 / Accepted: 27 November 2022 / Published online: 4 December 2022 © The Author(s) 2022

Abstract

The aggregate composed of cement clinker, an intermediate cement product, improves strength development and mass transfer resistance of concrete. Fly ash (FA) is a supplementary cementitious material that can be substituted by cement. This study investigated the strength development of highly FA-substituted mortar mixed with cement clinker fine aggregate (CL) and tested its inhibitory effect against the alkali–silica reaction (ASR). In addition to these, this study provides the testing results of evaluating the effects of using cement clinker fine aggregate on delayed ettringite formation (DEF), which can be problematic for precast concrete products. The study results revealed that at 91 days of age, in the case of 80% replacement ratio of fly ash to cement, using CL exhibited similar strength development as mortar with limestone fine aggregate and no FA substitution. Furthermore, mortars with 70% and 80% FA substitution did not exhibit clear ASR-induced expansion even at 182 days of age. Lastly, mortar using clinker fine aggregate could suppress DEF-induced expansion at 182 days of age, which was similar to the effect obtained using FA. These results can promote the utilization of CL resources for concrete and using clinker as fine aggregate in precast concrete products.

Keywords Clinker fine aggregate · Resource circulation · Alkali-silica reaction · Delayed ettringite formation

Introduction

In the cement manufacturing process, carbon dioxide is released, and the wastes and by-products produced in other industries are used as raw materials and heat energy. The "Long-term Vision of the Cement Industry Aiming for Carbon Neutrality" announced by the Japan Cement Association reported that the cement industry used approximately 27 million metric ton of waste in FY 2018, which comprised approximately 11% of the recycled resources of Japan, and this effort has contributed to the construction of a sound material cycle society [1]. In addition, it has been reported that waste plastics, which will be difficult to dispose of

Shintaro Miyamoto shintaro.miyamoto.b8@tohoku.ac.jp

¹ Department of Civil and Environmental Engineering, Graduate School of Engineering, Tohoku University, 6-6-06, Aramaki Aza Aoba, Aoba-Ku, Sendai, Miyagi 980-8579, Japan

² Taiheiyo Cement Corporation Central Research Laboratory, 2-4-2, Osaku, Sakura, Chiba 285-8655, Japan overseas in the future, can be used as a substitute for thermal energy, further contributing to the sound material cycle society. Moreover, according to the estimates by the Japan Cement Association, acceptance of waste and by-products in the cement industry is expected to extend the life of final industrial waste disposal sites by approximately 11 years [1].

According to the carbon neutral strategy developed by Global Cement and Concrete Association (GCCA), it is important to reduce the amount of cement clinker production to reduce CO_2 emissions [2]. On the other hand, the establishment of Carbon dioxide Capture, Utilization and Storage (CCUS) has the potential to greatly contribute to the reduction in CO₂ emission, and this technology is being developed as an essential technology for achieving carbon neutral in the cement and concrete fields. In addition, in Japan, on the website of the Agency for Natural Resources and Energy, it has been recommended that the CCUS in the clinker manufacturing process develop to achieve both reduction of CO₂ emissions and resource recycling in the cement industry [3]. If this technology is established, CO₂ emissions in the clinker manufacturing process will be reduced to almost zero. Therefore, it can be considered that clinker purely contributes to resource recycling if this technology is established in the future.

However, it is a fact that the domestic demand for cement is on the decline due to the maturation of social-infrastructure development. Therefore, if the clinker production were to shrink before CCUS was developed in the cement industry, more industrial waste would end up in landfills. To solve this problem, it is necessary to take new measures other than using cement as a binder to secure a certain amount of cement clinker production from the present.

Some research teams have focused on cement clinker, which is an intermediate product of cement, and investigated various basic physical properties of concrete and mortar that used cement clinker as a fine aggregate [3–5, 5]. These studies have clarified that mortar with cement clinker fine aggregate (CL) has excellent strength development and chloride ion transfer resistance [3]. Even when using fly ash (FA) as a binder, it could ensure the strength development of mortar using CL [5]. In addition, from the point of view of reducing the heat produced during the hydration reaction, the combination of FA and CL was valid [5].

However, alkali–silica reaction (ASR) mortar bar tests have shown that, when a part of cement was replaced by FA, mortars that used CL and andesite (An) as fine aggregate have a lower ASR-suppressing effect of FA than mortars that used limestone fine aggregate (LS) and An [5]. As per Miyamoto et al., it was considered that pH in a mortar increased due to the leaching of alkali from CL. Therefore, it was hypothesized that replacing cement with higher quantities of FA will lower the pH in mortar and improve an ASR-suppressing effect of FA. However, increasing the replacement ratio of FA may decrease the early age strength development of mortar.

Meanwhile, using CL increases the heat quantity associated with hydration [5]; therefore, it was considered that using CL can reduce the energy required for high-temperature steam curing for precast concrete (henceforth referred to as PCa). Furthermore, CL improves initial strength, which may enable early mould removal of PCa products. These advantages allow CL to support the dissemination of PCa products. Furthermore, the Ministry of Land, Infrastructure, Transport and Tourism has recommended the commercialization of PCa in concrete structures to improve productivity in the construction industry. In this regard, using CL is expected to contribute to resolving the labor shortage in the construction industry caused by the impending declining birth rate and aging population of Japan.

However, PCa products are a possibility that undergoes expansion and cracking due to DEF (Delayed Ettringite Formation.) DEF-induced expansion cracks can be occasionally seen on the hardened concrete which has a history of being subjected to high temperature during its hardening, such as high-temperature steam curing [6–9]. Expansion due to DEF is strongly related to the formation of ettringite as a secondary mineral. In addition to the high-temperature history of concrete, another factor that causes DEF is a decrease in pH of the pore solution. A pore solution of concrete has high pH at the time of manufacturing; however, pH of pore solution decreases over time in an environment where exposed by water. Ettringite tends to be produced at a pH of approximately 12, which is lower than the pH inside normal concrete [10–12], and decreased pore solution pH may promote the secondary formation of ettringite. Previous studies have shown that CL supplies alkali to pore solution [5]. Therefore, it was considered that pH of pore solution is possibility supress the decrease with this effect, thereby suppressing DEF.

Based on the above background, in this study, it was investigated that the strength development and ASR-induced expansion suppression effect of mortar that substituting cement by FA up to 80% and used CL. In addition, the DEFinduced expansion suppression effect of the mortar that used CL was verified in this study.

Experimental analysis

Materials

The binders used were Ordinary Portland Cement (OPC) manufactured by Taiheiyo Cement Corporation (density: 3.15 g/cm³, Blaine specific surface area: 3120 cm²/g) and FA (density: 2.27 g/cm³; Blaine specific surface area: 5190 cm²/g). Table 1 presents the chemical composition of OPC and FA. The fine aggregates used were ordinary Portland cement clinker (density in oven-dry condition: 2.72 g/cm³, percentage of absorption: 4.24%; CL), limestone crushed sand (density in oven-dry condition: 2.58 g/cm³, percentage of absorption: 1.85%; henceforth referred to as LS), and andesite (density in oven-dry condition: 2.57 g/cm³;

 Table 1
 Chemical composition

 of binder used
 Image: Chemical composition

Binder	Chemical composition (mass%)											
	L.O. I*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P_2O_5	MnO
OPC	2.45	20.96	4.93	3.08	64.18	0.90	1.97	0.32	0.34	0.31	0.49	0.08
FA	1.52	65.81	25.60	2.07	0.74	0.43	0.04	0.31	0.95	1.30	0.26	0.01

*L. O. I: Loss of ignition

 Table 2
 Mineral composition of clinker fine aggregate

Mineral composition (%)								
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	f.CaO*			
58.24	20.59	7.57	13.29	0.27	0.03			

*f. CaO: free CaO

percentage of absorption: 2.73%; henceforth referred to as An.) Here, An was used as the reactive aggregate for the expansion ratio test of ASR. Limestone may promote DEF-induced expansion [6]; therefore, in addition to LS, ISO standard sand conforming to ISO 679 (henceforth referred to as SS) manufactured by Japan Cement Association (density in oven-dry condition: 2.64 g/cm³, percentage of absorption: 0.42%, main components: SiO₂) was used for comparison in the DEF expansion ratio test. Table 2 presents the mineral composition of CL; Table 3 presents the chemical composition of CL, LS, and An; and Table 4 presents the mass fraction of the fine aggregates at each particle size range.

Mortar composition and preparation procedure

Three tests were conducted in this study: mortar compressive strength test, ASR expansion ratio test, and DEF expansion ratio test. Tables 5, 6, and 7, respectively, display the mix proportion of mortar in each test. Sample with CL as fine aggregate and FA substitution are expressed as "CL-FAXX", where "XX" represents the substitution ratio; for example, the sample with CL and an FA substitution ratio of 30% is described as CL-FA30. Samples with LS or SS as fine aggregate and no FA substitution are expressed as "LS-OPC" or "SS-OPC", respectively. Furthermore, the water/binder ratio (W/B) was uniformly set to 0.5; and fine aggregate/binder ratio (S/B) was set to 2.25 for CL and LS, and 3.0 for SS.

For the ASR expansion ratio test, with the purpose of promoting ASR, a 1 mol/L NaOH aqueous solution was prepared using a sodium hydroxide reagent (manufactured by Kanto Chemical Co., Inc., special grade) such that the alkali amount was adjusted to 1.20% Na₂Oeq with respect to the binder. Furthermore, the mixing ratio of An to fine aggregates was unified to a value of 30% based on a previous

 Table 4
 Mass fraction of fine aggregate at each particle size

Nominal sieve spi	read	Mass fraction (%)			
Passed	Residual	Fine aggregate			
4.75 mm	2.36 mm	10			
2.36 mm	1.18 mm	25			
1.18 mm	600 µm	25			
600 µm	300 µm	25			
300 µm	150 µm	15			

study [5] that reported a pessimum effect in which the expansion ratio was highest when the mixing ratio of An to the total aggregates was 30 mass%. For the DEF expansion ratio test, with the purpose of promoting DEF, potassium sulfate reagent (manufactured by Kanto Chemical Co., Inc., special grade) was added as well. The amount of potassium sulfate was referenced from previous studies at each level [9, 13] and set to 3% of the mass of OPC without FA substitution. In other words, a unit amount of 33 kg/m³ of potassium sulfate reagent was added to all samples in the DEF expansion ratio test.

The mixing method of mortar conformed to JIS R 5201 [14]. Because CL reacts with water, all fine aggregates were added in an oven-dry condition. Herein, the amount of water required for saturated surface condition was calculated from the percentage of absorption of each fine aggregate, and this amount of water was added to the mixing water. The mixed mortar was cast into a steel mould with internal dimensions of $40 \times 40 \times 160$ mm. The mould for the cast mortar samples was removed after 24 ± 2 h for the compressive strength test and ASR expansion ratio test. For the compressive strength test, samples removed from the moulds were subjected to underwater curing for up to 91 days in a constant temperature room set to 20 °C. The materials and water required for mixing were kept in the constant temperature room for at least 12 h before mixing. For the ASR expansion ratio test, the samples were placed in a closed container and kept at 95% R.H. or higher, followed by storage in an isothermal bath set to 40 °C for up to 182 days, in accordance with the mortar bar method specified in [17] [15]. R.H. of 95% or higher was maintained by filling water at the bottom of the container used for storing the sample, and laying a

Table 3	Chemical composition
of fine a	ggregate used

Aggregate	Chemical composition (%)											
	L. O. I	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	SO_3	Na ₂ O	K ₂ O	MgO	TiO ₂	P_2O_5	MnO
CL	0.61	21.72	5.99	3.25	64.78	1.43	0.45	0.3	0.36	0.35	0.55	0.08
LS	43.60	0.13	0.14	0.11	54.87	0.61	0.00	0.00	0.02	0.02	0.02	0.00
An	0.54	56.94	18.05	6.68	6.97	0.04	2.95	1.55	1.89	0.58	0.14	0.16

*L. O. I: Loss of ignition

Table 5 Mix proportion of mortar in compressive strength	Level	W/B	S/I	3	Unit amount (kg/m ³)					
tests					W	В			S	
						C	FA	_	LS	CL
	LS-OPC	0.5	2.2	25	299	597		0	1320	0
	CL-FA40				299	358	18	0	0	1392
	CL-FA50				299	299	22	5	0	1392
	CL-FA60				299	239	27	0	0	1392
	CL-FA70				299	179	31	5	0	1392
	CL-FA80				299	119	36	0	0	1392
Table 6 Mix proportion of mostar in ASP expansion ratio	Level	W/B	S/B	Unit am	ount (kg/r	n ³)				
tests				W	В		S			NaOH
					C	FA	LS	CL	An	
	LS-OPC	0.5	2.25	171	597	0	924	0	394	127
	CL-FA70			233	179	315	0	974	394	66
	CL-FA80			242	119	360	0	974	394	57
Table 7 Mix proportion of	Laval	W//P	S/D	Unit	amount (k	a/m^3				
mortar in DEF expansion ratio	Level	W/D	3/13			.g/m)				
tests				W	Bin	der	Sand			
					С	FA	1	LS	CL	SS
	SS-OPC	0.5	3	257	513		0	0	0	1533
	SS-FA30			257	359	11	6	0	0	1533
	LS-OPC		2.25	299	597	,	0	1320	0	0
	LS-FA30			299	418	13	5	1320	0	0
	CL-OPC			299	597	,	0	0	1392	0
	CL-FA30			299	418	13	5	0	1392	0

drainboard such that the sample would not come in direct contact with the water. Herein, in case that Na^+ and K^+ may be leached out of mortar if the specimen exposed in a humid container. In this case, if the specimen size was small such as in this study, it is cautioned that the expansion rate of ASR may be underestimated [16, 17].

For the DEF expansion ratio test, the sample was referred using the method described in previous research [18]. The curing method was as follows. At first, mortar that cast into a mould was cured at 20 ± 2 °C for four hours. Next, it was heated to 80 °C over a 3-h period at a heating rate of 20 °C/h. Thereafter, the sample was subjected to high-temperature curing for 10 h in an environment of 100% R.H. and 80 °C, followed by natural cooling to approximately 20 °C. Lastly, after 24 h, the mould was removed, and the mortar was subjected to water curing in an isothermal room set to 20 °C.

Overview of test method

Compressive strength test

After curing, the compressive strength test was conducted in accordance with JIS R 5201 [13] using both sections of the $40 \times 40 \times 160$ mm a prismatic sample cut into two pieces. For each case, six average compressive strength values were measured from three samples to calculate the compressive strength.

ASR expansion ratio test

The length of the mortar was measured after removing the mould, as well as at the ages of 14, 28, 56, 91, and 182 days. For measurement, the container in which the sample was placed on the previous day of each material age was moved

to a constant temperature room of 20 ± 2 °C and allowed to stand for at least 16 h; thereafter, the length of the sample was obtained using a micrometer. The sample length obtained after removing the mould was taken as the base length, and the change in length at each material age with respect to the base length was calculated as the expansion ratio.

DEF expansion ratio test

The length of the mortar was measured after the mould was removed, as well as at the ages of 14, 28, 56, 91, 119, 147, and 182 days. The length of the mortar was measured using a micrometer for samples that passed each material age. The calculation method for the expansion ratio was identical to that described in Sect. 2.3.2.

Results

Compressive strength test results

In the introduction, it was concerned that high volumes of FA substitution with OPC may reduce mortar strength. Therefore, this section examines the strength development of mortar in which high volumes of FA is substituted with OPC and CL is used.

Figure 1 shows the results of the compressive strength test up to the age of 28 days. As per the figure, the compressive strength decreased as the substitution ratio of FA with respect to OPC increased. However, CL-FA60 had a higher compressive strength than LS-OPC at an age of 28 days. Meanwhile, despite using CL, compressive strength of CL-FA70 and CL-FA80 were lower than that of LS-OPC at an age of 28 days. However, comparing CL-FA70,

CL-FA80, and LS-FA30 revealed a similar strength development in all three samples at an age of 28 days.

Figure 2 shows the results of the compressive strength test up to an age of 91 days for samples using CL as fine aggregate and an FA substitution ratio of 70% or 80%. As per the figure, the compressive strengths of both CL-FA70 and CL-FA80 were lower than that of LS-OPC at the age of 28 days: however, their compressive strength leveled to that of LS-OPC at an age of 91 days.

As per the above results, even at an FA substitution ratio of 60%, samples using CL as a fine aggregate exhibited better strength development than LS-OPC. In addition, even at an FA substitution ratio of 70% or 80%, setting a sufficient curing period resulted in a strength development that was equivalent to that of LS-OPC.

ASR expansion ratio test results

Figure 3 shows the results of the ASR expansion ratio test, and Fig. 4 shows the appearances of LS-OPC with expansion and CL-FA70 without expansion as representative samples at the age of 182 days after the test. As per Fig. 3, samples without FA substitution expanded more than 0.7% regardless of the aggregate type. In addition, as per Fig. 4, the LS-OPC with expansion leaked out a gel that was considered to be caused by ASR. Due to the influence of this phenomenon, cracks were observed more clearly. These results indicate that the expansion observed in this study was due to ASR. Furthermore, previously reported data [5] stated that expansion was certain suppressed in samples where 30% FA was substituted by cement, although it did not reach the level of "harmless" specified in [17] [15]. Therefore, it was confirmed that substituting FA with cement can suppress ASRinduced expansion.



Fig. 1 Compressive strength up to the age of 28 days



Fig. 2 Compressive strength up to the age of 91 days



Fig. 3 ASR expansion ratio test results

As per the previous report [5], ASR-induced expansion ratio was smaller for CL than that for LS when there was no FA substitution; however, this tendency was reversed when the FA substitution ratio was 30%. As mentioned above, Miyamoto et al. discussed that this was due to the increased pH in the mortar due to the leaching of alkali from CL, which hindered the ASR expansion suppression effect of FA. Therefore, it was hypothesized that substituting more FA for cement could lower the pH of the mortar and achieve sufficient an ASR suppression effect [5].

Based on this hypothesis of high-volume substitution FA to cement written in introduction, it was conducted that an ASR expansion ratio test using samples where the FA substitution ratio with respect to cement was 70% and 80%. As per the results, mortars with an FA substitution ratio of 70% or more did not expand clearly. In addition, as per Fig. 4, these mortars did not exhibit any gel leakage, which is thought to be caused by ASR. Therefore, an FA substitution ratio of 70% or more with respect to cement can obtain

sufficient ASR expansion suppression effect even when CL was used. Furthermore, as confirmed previously, these mortars had the same strength development as LS-OPC at an age of 91 days; therefore, with careful curing, an FA substitution ratio of 70% or 80% can provide a sufficiently practical countermeasure to ASR even if CL and reactive aggregate are mixed and used.

DEF expansion ratio test results

Figure 5 shows the DEF expansion ratio test results, and Fig. 6 shows the appearances of LS-OPC with swelling and CL-OPC without swelling as representative examples at the age of 182 days after the DEF expansion ratio test. As per Fig. 5, mortars that used SS and LS as fine aggregates started to expand after an age of 91 days, with an expansion



Fig. 5 DEF expansion ratio test results



(a) LS-OPC.

(b) CL-FA70.

Fig. 4 Sample appearance after the ASR expansion ratio test (age: 182 days)



Fig. 6 Sample appearance after the DEF expansion ratio test (age: 182 days)

of approximately 0.9% at an age of 182 days. As per Fig. 6, many fine cracks were generated on the LS-OPC surface.

Meanwhile, at the age of 182 days, no clear expansion behavior was observed in samples with 30% FA substitution that used SS, LS, and CL, and samples that used CL with only OPC as the binder. Furthermore, as per Fig. 6, CL-OPC did not exhibit the fine cracks. Kawabata et al. reported that the DEF-induced expansion can be suppressed by substituting 20% or more FA or 40% or more blast furnace slag fine powder with cement [19]. Correspondingly, in this study, although the observed age was only 182 days, the results indicate that the expansion caused by DEF can be suppressed by substituting 30% FA with cement. Additionally, the expansion caused by DEF may be suppressed at an age of 182 days even when CL is used.

Discussion

ASR-induced expansion suppression effect using CL and a binder with high FA substitution with cement

Previous reports [20, 21] have indicated that the suppression of ASR-induced expansion by FA generally involves reducing the amount of alkali contained in the cement matrix and lowering the pH of the pore solution. In this mechanism, dissolution of FA in the liquid phase supplies in a highly large amount of silicate ions but a small amount of Ca ions. Therefore. Ca ions derived from cement are used for C-S-H precipitation, and the concentration of Ca ions in the liquid phase decreases. In generally, Ca ions, which typically have a strong electrostatic interaction, are electrically adsorbed on the silanol group of C-S-H. However, in case that the concentration of Ca ions in the liquid phase is very low, Na and K ions are electrically adsorbed on the silanol group of C-S-H instead of Ca ions. As a result, the concentration of OH ions, which exists as a counter for Na and K ions, decreases as well, thereby decreasing the pH in the liquid phase [20], which in turn suppresses ASR. In other words, the adsorption of Na and K ions to C-S-H is inhibited when the concentration of Ca ion in the liquid phase is kept high, leading to insufficient ASR expansion suppression effect by FA. CL increases the Ca ion concentration in the liquid, which may reduce the suppression effect of FA on ASRinduced expansion.

Herein, Fig. 7 shows a backscattered electron image of the transition zone between CL and the cement matrix of CL-FA60 at an age of 91 days. In Fig. 7, it could be confirmed that the transition zone is dense, although the hydrated zone of CL is only the surface layer around CL and the large unhydrated zone remains in the interior. Therefore, it was considered that the supply of Ca ions from CL was to be stagnant after the age of 91 days. In addition to this, based on the results of the amount of leaching of Na and K ions from the clinker in case that CL was immersed in saturated calcium hydroxide solution [5], it was considered that the leaching of Na ion from CL almost converges after 91 days and the leaching of K ion from CL almost converges only few days. Therefore, it was considered that the influence of leaching of Na and K ions from CL was to be small after the age of 91 days.

Based on the above aspects, the following discussion is provided: if FA is substituted at a high ratio of 70% or more with cement, then the total amount of Na and K ions derived



Fig. 7 Backscattered electron image of the transition zone between CL and the cement matrix of CL-FA60 at an age of 91 days

from cement decreases even after the age of 91 days. Furthermore, it was considered that compared with the increase in the amount of Ca ions by using CL as the fine aggregate, the decrease in the amount of Ca ions due to a decrease in the amount of cement was effective. Therefore, ASR may be sufficiently suppressed because the pH in the system did not increase even when CL was used due to these factors. However, the actual pore volume and pH of the pore solution for mortar specimens were not measured in this experiment. Therefore, it was also considered important to measure these values directly.

DEF-induced expansion suppression effect of mortar that uses CL

It was shown in this study that using CL could suppress DEF-induced expansion as in the case of using FA. Although it was a qualitative evaluation, the molar ratio of the binder SO_3 and Al_2O_3 (SO_3/Al_2O_3 molar ratio) might be used as an indicator for evaluating the risk of DEF-induced expansion [18]. For the present study as well, the relationship between the SO_3/Al_2O_3 molar ratio and expansion ratio is summarized in Fig. 8 along with references to previously reported data [22, 23].

It can be seen from Fig. 8 that expansion occurred in the samples that did not use CL in the range of 1.0-1.3SO₃/Al₂O₃ molar ratio, including the previously reported data. However, CL-OPC, which had an SO₃/Al₂O₃ molar ratio in the same range, did not exhibit a clear expansion. These results indicate that the mechanism of suppressing DEF-induced expansion using CL might be different from the mechanism of ettringite production suppression due to decreased SO₃/Al₂O₃.



Fig. 8 Relationship between SO₃/Al₂O₃ and DEF

Kawabata et al. indicated that the DEF-induced expansion suppression effect of FA might be due to the improved mass transfer resistance in the system [19]. In addition, Miyamoto et al. reported that using CL improved the mass transfer resistance in mortar [3]. In addition, as shown in Fig. 7, When CL used for fine aggregate, the transition zone between the CL and the cement matrix is denser. Densification of the transition zone is effective in improving mass transfer resistance. Therefore, these results were considered that the suppression effect of CL on DEF-induced expansion was partly due to the improved mass transfer resistance in the mortar.

CL supplies Na and K ions into the system [5]. Exposing mortar to water results in the transfer of substances inside and outside the system. For example, exposing mortar to general water, such as tap water, results in a decrease the pH of the pore solution because Na and K ions are leached from the mortar. This phenomenon promotes secondary precipitation of ettringite because it approaches an environment where ettringite is more likely to be precipitated. Herein, Na and K ions are supplied from CL to the pore solution even when Na and K ions are leached from the mortar system. Therefore, the pH in the pore solution might remain high. In the present study, it was considered that this effect might contribute to the suppression of DEF-induced expansion as well. However, this is currently only a hypothesis; the expansion of the specimen must be observed over a longer period of time to prove it. This is because DEF-induced expansion is known to progress over the course of months to years. The present study set the age period to up to 182 days, which might have been a short period for investigating the expansion. As mentioned in Sect. 4.1, the influence of leaching of Na and K ions from CL might be small after the age of 91 days. Furthermore, as mentioned in Sect. 4.1, it is difficult to accurately determine the actual behavior occurring in the pore solution because the actual pore volume and pH of the pore solution for mortar specimens were not measured in this experiment. Therefore, investigations need to be continued comparisons must be made with results of FA-substituted samples to evaluate whether DEF-induced expansion suppression can occur over a long period of time when CL was used.

Conclusions

In this study, it was investigated that the effect of using CL in highly FA-substituted mortar on suppressing the expansion caused by alkali–silica reaction and delayed ettringite formation. The findings obtained are given below.

1. Suppression of ASR-induced expansion with a combination of CL and FA Using CL reduced the ASR suppression effect of FA compared to that of LS. However, using CL induced superior strength development relative to using LS; therefore, it is possible to substitute more FA for cement. In the scope of the present study, samples where CL was used and 80% of FA was substituted with cement had similar strength expression to that of FA-free mortar using LS at an age of 91 days. Additionally, mortar with an FA substitution ratio of 70% and 80% did not show clear expansion in the mortar bar method that was specified in [17], even at an age of 182 days. Therefore, ASR-induced expansion might be sufficiently suppressed by substituting more FA for cement, even when the CL is used.

This technology will be able to achieve effective utilization of aggregate resources that were not utilized in the past by compensating the lack of particle size of the reactive aggregate with clinker fine aggregate and suppressing the risk of deterioration due to ASR with using FA, such as cases when it is necessary to utilize reactive aggregate that does not meet the particle size standard in an environment where obtaining high-quality natural aggregate is challenging.

2. Suppression of DEF-induced expansion using clinker fine aggregate

The present study showed that using CL can suppress DEF-induced expansion, as in the case of using FA. This reason was considered that the mass transfer resistance in the mortar was improved caused by using CL. In addition, it was considered that the pH in the system might remain high caused by supplying Na and K ions from CL.

However, these data presented in this study are at ages of 182 days, and the expansion behavior needs to be observed over a longer period of time. However, DEF-induced expansion can be suppressed at an age of 182 days. Furthermore, using CL can improve initial strength development of product, thereby allowing early removal from moulds. Therefore, it can be expected to be applied to precast concrete products in the future.

Acknowledgements This study was supported by JSPS KAKENHI Grant Number JP19H02209. We would like to express our sincere gratitude to the reviewers. In addition, we would like to thank Editage (www.editage.com) for English language editing.

Data availability statement All data generated or analysed during this study are included in this published article and its supplementary information files.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes

were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

- Japan Cement Association, Long-term Vision of the Cement Industry Aiming for Carbon Neutrality, https://www.jcassoc. or.jp/cement/4pdf/220324_01.pdf. Accessed 18 Apr 2022 (in Japanese)
- Global Cement and Concrete Association: Concrete Future the GCCA 2050 Cement and Concrete Industry Roadmap for Net Zero Concrete. https://gccassociation.org/concretefuture/wp-conte nt/uploads/2021/10/GCCA-Concrete-Future-Roadmap-Docum ent-AW.pdf. Accessed 22 Aug 2022
- Agency for Natural Resources and Energy Home Page. https:// www.enecho.meti.go.jp/about/special/johoteikyo/concrete_ cement.html. Accessed 22 August 2022 (in Japanese)
- Miyamoto S, Inada H, Minagawa H, Hisada M (2015) Influence of using cement clinker as fine aggregate on the properties of mortar. Cement Sci Concrete Technol 69(1):169–175 (in Japanese with English abstract)
- Berger RL (1974) Properties of concrete with cement clinker aggregate. Cem Concr Res 4(1):99–112
- Shafaghat J, Allahverdi A (2020) Using PC clinker as aggregateenhancing concrete properties by improving ITZ microstructure. Mag Concr Res 72(4):173–181
- Miyamoto S, Hayashi K, Naruse D, Hosokawa Y, Minagawa H, Hisada M (2022) Verification of the mutually complementary effect of fly ash and clinker aggregate on the strength, heat of hydration and alkali silica reaction. J Mater Cycles Waste Manage 24(4):1396–1406
- Fu Y, Xie P, Gu P, Beaudoin JJ (1994) Significance of pre-existing cracks on nucleation of secondary ettringite in steam cured cement paste. Cem Concr Res 24(6):1015–1024
- Taylor HFW, Famy C, Scrivener KL (2001) Delayed ettringite formation. Cem Concr Res 31(5):683–693
- Zhang Z, Olek J, Diamond S (2002) Studies on delayed ettringite formation in early-age, heat-cured mortars I. Expansion measurements, changes in dynamic modulus of elasticity, and weight gains. Cement Concrete Res 32:1729–1736
- Kawabata Y, Ogawa S, Takahashi H, Sagawa Y (2015) Evaluation of influencing factors for DEF expansion based on long-term laboratory tests. Cement Sci Concrete Technol 69(1):527–534 (in Japanese with English abstract)
- Damidot D, Glasser FP (1992) Thermodynamic investigation of the CaO-Al₂O₃-CaSO₄-H₂O system at 50 °C and 85 °C. Cem Concr Res 22(6):1179–1191
- Damidot D, Glasser FP (1993) Thermodynamic investigation of the CaO-Al₂O₃-CaSO₄-H₂O system at 25 °C and the influence of Na₂O. Cem Concr Res 23(1):221–238
- Stark J, Bollmann K (1999) Delayed ettringite formation in concrete. Nordic Concrete Federation 23(2):4–28
- Kelham S (1996) The effect of cement composition and fineness on expansion associated with delayed ettringite formation. Cement Concr Compos 18(3):171–179
- 16. JIS R 5201, Physical testing methods for cement, ver., 2015 (in Japanese)
- 17. JIS A 1146, Method of test for alkali-silica reactivity of aggregates by mortar-bar method, ver., 2017 (**in Japanese**)

- Lindgård J, Thomas MDA, Sellevold EJ, Pedersen B, Çakır ÖA, Justnes H, Rønning TF (2013) Alkali–silica reaction (ASR)—performance testing: Influence of specimen pre-treatment, exposure conditions and prism size on alkali leaching and prism expansion. Cement Concrete Res 53:68–90
- Yamada K, Karasuda S, Ogawa S, Sagawa Y, Osako M, Hamada H, Isneini M (2014) CPT as an evaluation method of concrete mixture for ASR expansion. Constr Build Mater 64:184–191
- Odler I, Chen Y (1995) Effect of cement composition on the expansion of heat-cured cement pastes. Cem Concr Res 25(4):853-862
- 21. Kawabata Y, Takahashi H, Watanabe S (2021) The long-term suppression effects of fly ash and slag on the expansion of heat-cured mortar due to delayed ettringite formation. Constr Build Mater 310:125235

- 22. Thomas M (2011) The effect of supplementary cementing materials on alkali-silica reaction: a review. Cem Concr Res 41(12):1224–1231
- 23. Kawabata Y, Yamada K (2017) The mechanism of limited inhibition by fly ash on expansion due to alkali–silica reaction at the pessimum proportion. Cem Concr Res 92:1–15
- Tosun K (2006) Effect of SO₃ content and fineness on the rate of delayed ettringite formation in heat cured Portland cement mortars. Cement Concr Compos 28(9):761–772
- Fu Y, Ding J, Beaudoin JJ (1997) expansion of portland cement mortar due to internal sulfate attack. Cem Concr Res 27(9):1299–1306

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.