Study on the properties of mortar using ordinary portland cement clinker as fine aggregate

Tayuto kikuchi[1], Hiromi Fujiwara[1], Masanori Maruoka[1], Arato Kobayashi [1], and Kensuke Hayashi[2]

[1]Graduate School of Regional Development and Creativity, Utsunomiya University / Utsunomiya, Tochigi, Japan
[2]Central Research Laboratory of Taiheiyo Cement Corporation. / Sakura Chiba Japan

Abstract: The cement industry in Japan has been using industrial waste and by-products as raw materials in the production of cement clinker. In recent years, there has been little increase or decrease in waste generation in Japan. However, domestic demand for cement has been declining. It is important to maintain the amount of waste received by the cement industry in order to reduce the industrial waste. Therefore, it is necessary to develop new uses for clinker other than cement. In this study, it was investigated the properties of mortar using ordinary Portland cement clinker as fine aggregate. In addition, in order to improve fresh properties, gypsum anhydride was mixed as a binder. In the hardened mortar tests, clinker for ordinary Portland cement was replaced by 0%, 25%, 50%, 75%, and 100% by volume with respect to fine aggregate. Increasing substitution ratio. increased compressive strength and reduced drying shrinkage were confirmed. The fresh properties test results showed that adding anhydrous gypsum was effective to improve the flowability of the mortar at low substitution rates.

Keywords: clinker,fine aggregate,anhydrite flowability.

1. INTRODUCTION

Currently uses various industrial wastes and by-products as raw materials to produce cement clinker. There has been little change in the amounts of such wastes produced in recent years but, as shown in **Figure-1**, domestic demand for cement is decreasing. Therefore, in order to continue using waste effectively, it is necessary to consider new and expanded uses for cement clinker. Generally, the raw materials of cement, such as limestone, clay, silicate, and iron oxide, are fired in a rotary kiln or other kiln at temperatures up to about 1500°C and then quenched to form fist-sized lumps. This clinker is ground into cement by adding an appropriate amount (2-3%) of gypsum. The objective of this project is to improve waste utilization in the cement industry by investigating new ways to use clinker and to increase the amount of clinker used and produced.Clinker is an intermediate product of cement and therefore has hydraulic properties similar to those of cement and other materials. Previous studies have shown that clinker, when used as a fine aggregate in mortar and concrete, is self-healing. Contact with water after cracks or other deteriorations have occurred due to external action initiates a hydration reaction because of its hydraulic hardness[1] [2]. Based on this previous work, the applicability of mortar using clinker as fine aggregate as a material for cross-section repairs has been investigated. Such a use of ordinary Portland cement clinker to repair the cross section of concrete structures would reduce the accelerated deterioration of mortar and concrete by external actions such as frost damage and chemical erosion, which are considered factors with a significant impact on durability. This would promote the self-healing of deteriorated areas and ensure long-term utility.

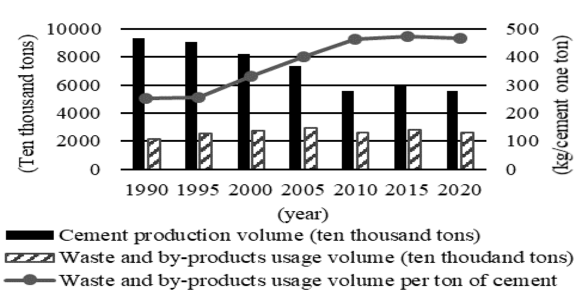


Fig. 1 Trends in waste and by-product usage in the cement industry

2. *Basic Properties of Mortar Using Ordinary Portland Cement Clinker as Fine Aggregate*

2.1 Materials used

Ordinary Portland cement (symbol: C; density: 3.15 g/cm^3) was used as the binder. Tohoku silica sand No. 4 (symbol: SS; surface dry density: 2.61 g/cm^3) and ordinary Portland cement clinker (symbol: NCL; absolute dry density: 2.60 g/cm^3) were used as fine aggregate. The particle size distribution of the NCL fine aggregate was adjusted to be similar to that of the Tohoku silica sand No. 4. This is shown in **Figure-2.** Tap water (W), a high-performance AE reducer (SP), and a defoaming agent (DF) were used in the mixes. The mineralogical structure of the NCL is shown in **Table-1**.

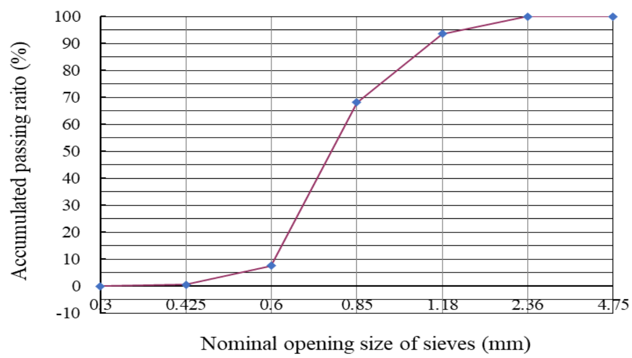


Fig. 2 Particle size distribution of fine aggregate

Table 1. Mineral composition of clinker

Symbol	Mineral composition(%)					
	C_3S	C_2S	C_2AS	$C_{12}A_7$	C_3A	C_4AF
NCL	62	15	0	0	9	10

2.2 Mix Proportions

Table-2 shows the planned mix proportions used in this study.The target 0 stroke flow and air content are 250±25 mm and 2.0%, respectively.

Table 2. mortar mix proportions (fundamental property experiments)

Symbol	NCL/S (%)	W/C (%)	unit weight(kg/m^3)			
			W	C	SS	NCL
NCL0%	0	30	268	893	1122	0
NCL25%	25				842	292
NCL50%	50				561	585
NCL75%	75				281	876
NCL100%	100				0	1169

2.3 Test Methods

Tests were carried out on the mortar as follows.

2.3.1 Fresh property test

0 stroke flow test were conducted in accordance with ISO 679 and air content tests in accordance with ISO 1920-2

2.3.2 Compressive strength test

Compressive strength tests were performed according to ISO 1920-4. The strength was measured after 7 days and 28 days of curing in water at 20°C. The test specimens were 50 mm in diameter and 100 mm in height. Three specimens were used for each condition.

2.3.3 Drying shrinkage test

Drying shrinkage was measured in accordance with ISO 1920-8. The specimens used for testing were three were used for each condition. Measurement began after 7 days of curing in water at 20°C. Drying conditions were 20°C and 60% humidity.

2.3.4 Salt immersion test

This test was performed using the silver nitrate solution spray method. The silver nitrate solution spray method uses a reaction in which a white silver chloride precipitate is formed when chloride ions are added to a silver nitrate solution. Specimens measuring 100 mm × 100 mm × 100 mm were cured in water at 20°C for 28 days. The specimens were immersed in a 10% NaCl solution at a temperature of 20±2°C for 28, 48, and 91 days, respectively, and the salt immersion areas were measured. On the day of measurement, the specimens were removed from the NaCl solution and cut 30 mm from one end with a cutter. The cut surface was sprayed with 0.1 mol/L silver nitrate solution, and the area emitting fluorescence at the outer edge was measured at 10 locations per sample as the chloride ion penetration area, the average of which was calculated, and the distance was defined as the depth of chloride ion penetration.

2.3.5 Adhesion test

Adhesion tests were conducted in accordance with JSCE K 561:2003, "Testing Methods for Section Repair Materials for Concrete Structures (Draft), 5.8 Adhesion Strength". The experimental procedure is described below.

①Treat the surface of the form face of the concret substrate board using No. 150 abrasive paper specified in JIS R 6252.
② Apply the cross section repair material to a concrete substrate (300 x 300 x 60 mm) with a trowel to a thickness of 10 mm.
③ Cure in a curing room at a temperature of 20±2°C for up to 28 days, depending on the age of the material.
The following is shown in **Figure-3.**
④ Make a 40 x 40 mm, 10 mm deep cut with a cutter, attach the steel adhesive jig to the cut with epoxy resin adhesive, and wipe off any excess adhesive around the cut.
⑤After confirming the adhesion, conduct a uniaxial tensile test, paying attention to eccentricity. For this uniaxial tensile test, use a simple hydraulic tensile tester approved by the Japan Society of Building Finishing Engineers. The test shall be conducted 6 times for one board.
⑥The bond strength A (N/mm2) shall be obtained by the following formula and rounded off to two decimal places.

$$A = \frac{P}{S} \tag{1}$$

A: Adhesion strength (N/mm2)
P: Maximum tensile load (N)
S：Surface area of adhesion (mm2)

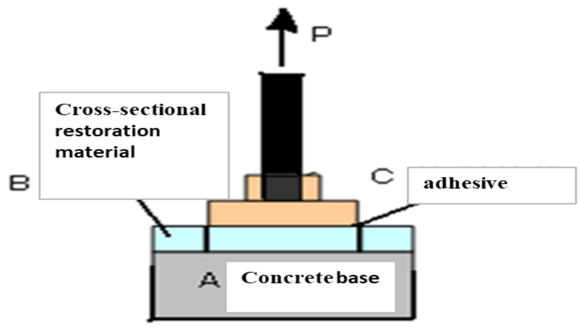


Fig.3 Adhesion Test Procedure

2.4 Test Results and Discussion

2.4.1 Fresh property test

The results of the fresh property test are shown in **Table-3**. 0%, 25%, and 50% obtained the target flow, respectively. However, 75% NCL and 100% NCL could not obtain sufficient flow even at 4% SP addition, which is the upper limit recommended by the manufacturer. Therefore, specimens of 75% NCL and 100% NCL were prepared with the same admixture addition rate as that of 50% NCL for comparison with 50% NCL.

2.4.2 Compressive strength test

The results of compressive strength tests are shown in **Figure-4**. Compressive strength tends to increase as the NCL replacement ratio increases. Hosoda et al. have previously reported that when clinker is used as aggregate, the aggregate interface becomes denser due to a progressive hydration reaction[3], possibly because the hydration reaction takes place at the NCL surface. This higher density at the aggregate interface increases the bond strength at the interface compared with the case where silica sand is used.

Table 3. Fresh property test results

NCL/S(%)	SP(%)	DF(%)	Air(%)	flow(mm)
0	1.1	0.1	0.4	240
25	1.2	0.1	0.4	250
50	2.0	0.4	0.8	265
75	2.0	0.6	2.3	210
100	2.0	0.4	1.4	100

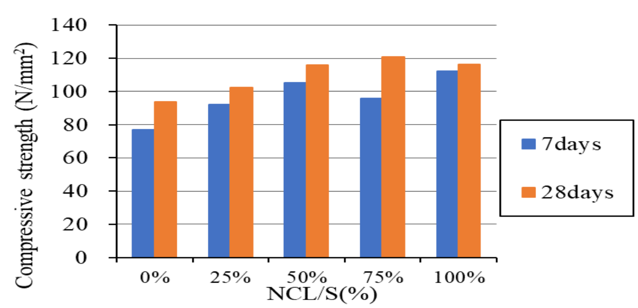


Fig.4 Compressive strength test results

2.4.3 Drying shrinkage test

The results of drying shrinkage tests are shown in **Figure-5**. Although the difference in dimensional change between 0% NCL and 25% NCL is small, it is confirmed that drying shrinkage is reduced in all formulations with NCL. This is thought to be due to the hydration reaction of NCL, which improves the structure of the transition zone at the boundary between aggregate and cement paste, resulting in a denser structure and therefore less drying shrinkage. Uchikawa has reported that the formation of a transition zone where the pores have a diameter of 50 nm to 2 μm increases drying shrinkage, and the results of this test also suggest that the use of NCL improves the transition zone of the hardened mass. [4]

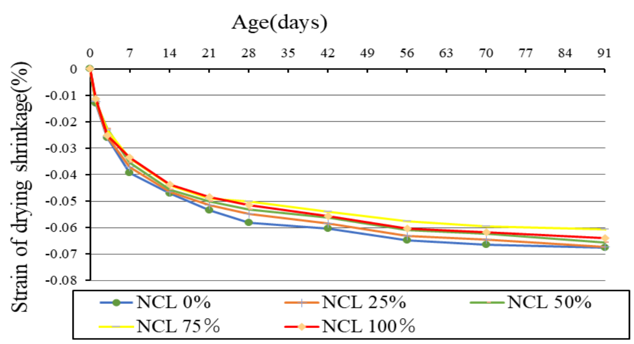


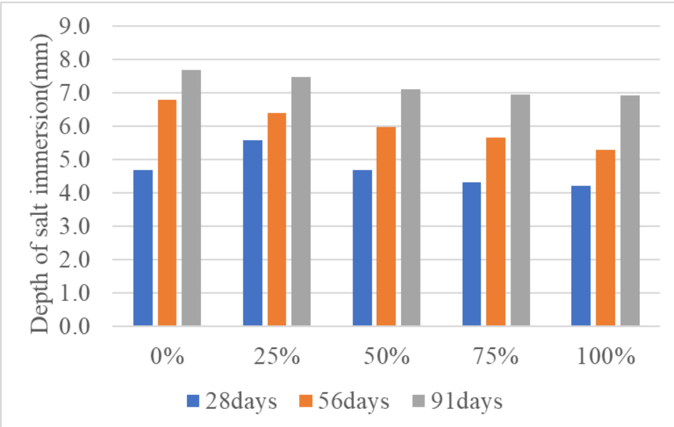
Fig.4 Drying shrinkage test results

2.4.4 Salt immersion test

The results of the salt immersion tests are shown in **Figure-6**. The results show that the diffusion of chloride ions tends to be suppressed as the NCL replacement ratio increases, although only slightly. This may be due to the fact that the cement pastes or the transition zones become more dense with the presence of NCL due to the additional hydration reaction reported by Hosoda et al. and suggested in the previous section. [5] The denser transition zones make it more difficult for chloride ions to penetrate into the mortar. It is also possible that immobilization of chloride ions may occur through the formation of Friedel's salt.

2.4.5 Adhesion test

The results of the adhesive strength test are shown in **Figure 7**. Adhesive strength tests were conducted at six locations each. Some samples could not be measured correctly because the adhesive used for the steel adhesive jig peeled off. This peeling was the result of the adhesive no longer being able to withstand the test load. In the case of the mortar using Tohoku Silica Sand No. 4, no clear trend in adhesive strength was obtained compared to 0% NCL, but similar adhesive strength was confirmed for both formulations. The aforementioned results suggest that hydration of the NCL fine aggregate in the mortar may reduce the fragile layer and improve adhesion to the substrate, but no such trend was observed in this test. In addition, the specimens that failed mostly or completely did not fail at the point of adhesion to the substrate, suggesting that the adhesive strength was greater than the loads reached in these tests.



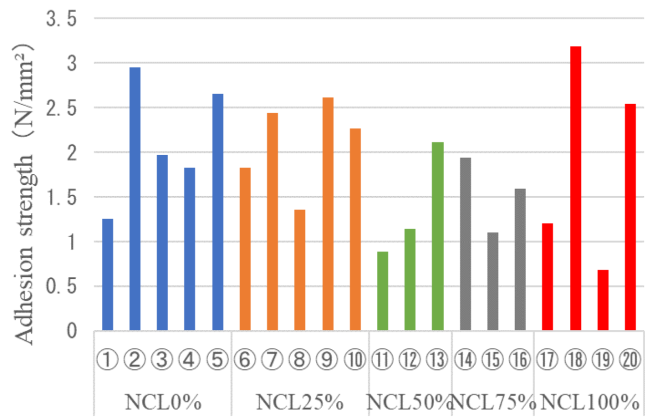


Fig.6 *Salt immersion test* results

Fig.7 Adhesion test results

3. Investigation on the Effectiveness of Anhydrite Admixture of Mortar with Clinker Fine Aggregate for Ordinary Portland Cement in Improving Fresh Properties of Mortar

In the tests described in section 2, the target flow value could not be obtained with a high clinker fine aggregate replacement ratio. It was inferred that the reason for this low flowability was the rapid setting of aluminate (C_3A) and ferrite (C_4AF) contained in the ordinary Portland cement clinker, so an improvement in flowability was attempted by adding anhydrite, which is also used to delay rapid setting of cement. That is, we attempted to improve fluidity by adding anhydrite to the mortar mix.

3.1 Materials used

The materials used in these additional tests were ordinary Portland cement (symbol: C; density: 3.15 g/cm3) and anhydrite gypsum (AG) as binders, silica sand No. 4 (symbol: SS; dry density: 2.61 g/cm3; F.M.: 2.91; water absorption: 1.48%) as fine aggregate, and ordinary Portland cement clinker (symbol: NCL; absolute dry density: 2.60 g/cm3) were used. AG was substituted for cement at a ratio of 5% by mass. Tap water (symbol: W) was used as the mixing water. The particle size distribution of the fine aggregate was adjusted to be the same as that in **Figure 2.**

3.2 Mix Proportions

Table-4 shows the planned mix proportions used in this study.The target 0 stroke flow and air content are 250±25 mm and 2.0%, respectively.

Table 4. Mixing ratio of mortar mixed with anhydrous gypsum (basic physical properties experiment)

NCL/S(%)	W/B(%)	unit weight(kg/m3)				
		W	B		SS	NCL
			C	AG		
0	30	268	848	45	1122	0
25					842	292
50					561	585
75					281	876
100					0	1169

3.3 Mix Proportions

Fresh properties tests, consisting of 0 stroke flow tests and the air content tests, were carried out as described in section ***2.3.1***

3.4 Test Results and Discussion

The results of the fresh property test with anhydrous gypsum admixed are shown in **Table-5**. The only anhydrite admixture formulation for which the target flow value could not be obtained was 100% NCL. Further, with this formulation, water separation was observed because of the high ratio of SP to cement. The target 0 stroke flow was not obtained for NCL 75% without anhydrite admixture, but the addition of anhydrite allowed the target flow value to be reached. In addition, the required amounts of SP for NCL 0% to 75% were reduced with the addition of the anhydrite admixture. This suggests that flowability was improved.

Kondo et al.showed that gypsum forms an insoluble hydration film on the particles of water-soluble, rapid-condensing substances such as C3A and C4AF, reducing the hydration rate of clinker at a very early stage. [6] As soon as the cement comes into contact with water, C3A undergoes an exothermic reaction that results in instantaneous setting, but the addition of gypsum to the cement prevents this rapid setting. As soon as the gypsum dissolves in water, it forms a thin layer of hydrate on the cement surface, preventing hydration of the cement for 1-3 hours, during which time needle-like crystals of ettringite are formed. After the formation of ettringite, C3S reacts to form tobermorite, a stable hydrate. About three days after the C3A reaction, C2S begins to react to produce tobermorite in the same manner as C3A. This tobermorite is also gelatinous at first, filling the gaps between the needle-like crystals, before it crystallizes to reach about 80% of its final strength at about 28 days of age. It is assumed that this effect was also present in this study.

Kondo et al reported that the appropriate amount of gypsum to add to the cement is around 3%, regardless of the form of the gypsum. [7] The gypsum addition rate in the formulations tested in this section was calculated assuming that NCL used as fine aggregate is the same substance as cement. The ratio of gypsum to cement (Portland cement + NCL) in the mortar was calculated by taking into account the amount of anhydrous gypsum mixed with 5% of cement and the gypsum content added in advance to the ordinary Portland cement used, as shown in the table. The table shows that the percentage of gypsum in 100% NCL is around 3%, which is close to the appropriate amount reported by Kondo et al., but the target 0 flow value could not be obtained. From these results, it was judged impossible to improve the fresh properties only by suppressing initial hydration through the addition of anhydrite. This means it is necessary to take other measures to improve flowability, such as improving the aggregate particle shape.

Table 5. Fresh property test results

NCL/S(%)	SP(%)	DF(%)	Air(%)	flow(mm)
0	0.8	0.1	1.5	240
25	1.1	0.3	1.0	250
50	1.5	0.4	0.8	265
75	1.8	0.4	1.7	240
100	2.1	0.4	1.7	140

4. Conclusion

In this study, researchers investigated the properties of concrete containing NCL as fine aggregate. Based on the results of the study, the following conclusions can be drawn.

Compared to mortar without NCL, compressive strength is increased and drying shrinkage is reduced. Diffusion of chloride ions was also suppressed and adhesion strength was confirmed. However, bleeding increased as the proportion of NCL increased. This may affect flowability and curing properties, and further study of this effect is needed in the future.

When anhydrite admixture was not mixed, a target 0 stroke flow was not obtained for 75% NCL, but when anhydrite admixture was mixed, a target 0 stroke flow was obtained, suggesting a slight improvement in flowability. However, the target 0 stroke flow could not be obtained only for 100% NCL. Looking ahead, we need to take other measures to improve flowability, such as improving the particle shape of the aggregate.

5. Acknowledgement

I would like to express my deepest gratitude to all those who assisted me in conducting the experiments and writing the thesis.
I would like to express my deepest gratitude to Dr. Hiromi Fujiwara, Professor of the Graduate School of Engineering, Utsunomiya University, for providing me with the opportunity to conduct this research and for his basic and easy-to-understand guidance in the preparation of this thesis. Dr. Masanori Maruoka, Associate Professor at the Graduate School of Engineering, Utsunomiya University, gave me a lot of advice in conducting experiments. We would like to express our sincere gratitude for his cooperation.Mr. Kensuke Hayashi of Taiheiyo Cement Corporation took time out of his busy schedule to provide us with a great deal of advice and knowledge related to our research.I also received generous support in various ways from my seniors, peers, and juniors in the laboratory, including my family. Thanks to all of you, I was able to devote myself to my research and submit this thesis. Finally, I would like to express my deepest gratitude to all of you for your cooperation.

6. References

［1］S. Ito, H. Fujiwara, M. Maruoka, K. Hayashi: Study on Evaluation of Self-Healing Performance of Concrete Using Various Clinkers as Fine Aggregate, Proceedings of the Japan Concrete Institute Vol.41, No1, 2019, pp1415-1420

［2］［3］［5］S. Hosoda, M. Watanabe, T. Higuchi, M. Morioka: Densification and self-healing function of mortar by clinker fine aggregate, Cement & Concrete Journal, No.67, pp.187-194, 2013

［6］ R.Kondo: Utilization of anhydrous cement, Gypsum & Lime, No.43, 1959

［7］ R. Kondo and S. Yamauchi: Appropriate form and amount of gypsum added to cement, Kiln Association, 63 (705), 1955