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Abstract: In recent years, efforts to reduce greenhouse gas emissions have continued worldwide. In the construction industry, a large amount of CO₂ is generated during the production of Portland cement, and various studies are being conducted to reduce the amount of cement and enable the use of cement substitutes. Ferronickel slag is a by-product generated by melting materials such as nickel ore and bituminous coal, which are used as raw materials to produce ferronickel at high temperatures. In this study, we investigated the fluidity, microhydration heat, compressive strength, drying shrinkage, and carbonation characteristics of a ternary cement mortar including ferronickel-slag powder and fly ash. According to the test results, the microhydration heat of the FA20FN00 sample was slightly higher than that of the FA00FN20 sample. The 28-day compressive strength of the FA20FN00 mix was approximately 39.6 MPa, which was higher than that of the other samples, whereas the compressive strength of the FA20FN15 mix including 15% of ferronickel-slag powder was approximately 11.6% lower than that of the FA20FN00 mix. The drying shrinkage of the FA20FN00 sample without ferronickel-slag powder was the highest after 56 days, whereas the FA00FN20 sample without ferronickel-slag powder to the other mixes.

Keywords: fly ash; ferronickel slag; microhydration heat; compressive strength; drying shrinkage; carbonation depth

1. Introduction

In recent years, efforts to reduce greenhouse gas (GHG) emissions have continued worldwide. In Korea, the government has established a roadmap for GHG reduction based on prescribed target values to be fulfilled [1]. In the construction industry, Portland cement is widely used to produce ready-mixed concrete and precast concrete products. However, a large amount of CO_2 is generated during the production of Portland cement, and various studies are being conducted to reduce the amount of cement and enable the use of cement substitutes [2–5]. Among industrial by-products, fly ash generated in thermal power plants has a pozzolanic reaction and is widely used in concrete. Specifically, in Korea, approximately 10 to 20% of fly ash is substituted for cement content in readymixed concrete [6]. In addition, various steel industry by-products are widely used in the construction industry. Ferronickel slag is a by-product generated by melting materials such as nickel ore and bituminous coal, which are used as raw materials to produce ferronickel at high temperatures. More than 2 million tons are yearly generated in South Korea [7]. To use ferronickel slag in the construction industry, several guidelines and standards were established [8–10], but the recycling rate is still insignificant, and ferronickel slag that has not been recycled is buried and neglected in yards, causing environmental pollution [11]. As an effort to increase the recyclability and value of ferronickel slag, some studies proposed to convert ferronickel slag into fine powder and use it as a cement substitute [12–14].

Kim et al. [12] reported that fine ferronickel-slag powder can fill the voids in paste; the higher the replacement rate of this fine ferronickel-slag powder, the lower the chloride ion



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penetration. According to a study by Kim et al. [11], ferronickel slag is effective in reducing the hydration heat and drying shrinkage of cement mortar when ferronickel-slag powder is used as a cement substitute.

In addition, in a study by Cho et al. [13], it was reported that the mixing of ferronickelslag powder contributes to achieve tight pore structures in the cement matrix.

Interestingly, it was also reported that the drying shrinkage of cement mortar is reduced when used with other mineral admixtures, in contrast with using ferronickel-slag powder alone [14].

Although a number of studies focused on recycling ferronickel slag, few addressed the use of ferronickel-slag powder and fly ash together. The combination of ferronickel slag and fly ash to achieve good engineering performance of cement mortar is expected to contribute to the increase in recycling of both materials. This study evaluates the compatibility between ferronickel-slag powder (FN) and fly ash (FA) when FA is mixed with FN at a certain ratio to increase the recycling rate of FN, which remains insignificant compared with other steel industry byproducts. The ultimate goal is to reduce environmental pollution by increasing the recycling rate of steel industry byproducts. In this study, we investigated the fluidity, microhydration heat, compressive strength, drying shrinkage, and carbonation characteristics of a ternary cement mortar using ferronickel-slag powder and fly ash as part of a study to increase the recycling of ferronickel slag.

2. Materials and Methods

2.1. Materials

In this study, ordinary Portland cement (OPC) manufactured by Asia Co., Ltd. in Korea, and fly ash manufactured at the D thermal power plant in Korea were used. To achieve ferronickel-slag powder, a ferronickel-slag aggregate generated by the S Company in Korea was pulverized using a ball-mill (Blaine 3550 cm²/g). Figures 1 and 2 show the state and SEM images of the fly ash and ferronickel-slag powder used in this study. Unlike fly ash, which has a spherical shape, the ferronickel-slag powder exhibits an irregular grain shape. Table 1 shows the chemical compositions of the cementitious materials used in this study. To achieve a fine aggregate, sand from Namwon, Korea, with a specific gravity of 2.6 and a fineness modulus of 2.89 was used.



Figure 1. Fly ash and ferronickel-slag powder sample: (a) fly ash, (b) ferronickel-slag powder.



Figure 2. SEM images of sample: (a) fly ash, (b) ferronickel-slag powder.

Туре	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Blaine (cm ² /g)
Cement	17.43	6.50	3.57	64.40	2.55	1.17	3430
Ferronickel-slag powder (FN)	48.91	2.08	11.6	0.82	32.41	0.09	3550
Fly ash (FA)	64.88	20.56	6.06	2.58	0.80	1.45	3710

2.2. Mixing Proportions and Specimen Preparation

Table 2 shows the mix proportions of cement mortar. To examine the compatibility of the most commonly used fly ash and ferronickel-slag powder, both materials were replaced by 20% of the cement weight. The replacement ratios of fly ash were 20% (FA20FN00), 15% (FA15FN05), 10% (FA10FN10), 5% (FA05FN15), and 0% (FA00FN20). The water-to-cementitious material ratio was fixed at 50%. Moreover, 50 mm cube specimens were prepared for compressive strength test, and $40 \times 40 \times 160$ mm specimens were prepared for drying shrinkage and accelerated carbonation test. Then, we demolded the specimen after 24 h and cured it in a water tank at 20 °C until reaching the required age. In addition, the microhydration–heat test was performed using MMC-511SV6 of Tokyo Riko Co. Ltd. for FA20FN00 (FA 20%), FA10FN10 (FA 10%), and FA00FN20 (FA 0%) samples. The microhydration heat was measured for up to 72 h after fabrication by the multi-micro-calorimeter test method.

Table 2. Mix	proportions.
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Mix.	FA (%)	FN (%)	W/Cm (%)	W (kg/m ³)	C (kg/m ³)	FA (kg/m ³)	FN (kg/m ³)	Sand (kg/m ³)
FA20FN00	20	0				68	0	902
FA15FN05	15	5				51	17	906
FA10FN10	10	10	50	170	272	34	34	909
FA05FN15	5	15				17	51	912
FA00FN20	0	20				0	68	915

Mortar flow and compressive strength were measured according to KS L 5105 [15], and drying shrinkage was measured according to KS F 2424 [16]. Concerning the carbonation test, the carbonation depth was measured using a phenolphthalein solution once the carbonation process finished in an accelerated carbonation chamber according to KS F 2584 [17].

3. Results and Discussion

3.1. Microhydration Heat

Figure 3 shows the microhydration–heat change in the ternary cement mortar using ferronickel-slag powder and fly ash. Note from the figure that the difference between the microhydration heat of the three mixes was not large. The microhydration heat of the FA20FN00 mix including only fly ash (63.04 cal/g) was slightly higher than that of the FA00FN20 mix including only the ferronickel-slag powder (61.88 cal/g). This is similar to the results reported in previous research results [13], that is, the microhydration heat is relatively low in the mix including ferronickel-slag powder. It is supposed that the use of ferronickel-slag powder can reduce the hydration heat of mortar and concrete. The microhydration heat of the FA10FN10 mix including ferronickel-slag powder and fly ash was equal to or less than that of FA20FN00 mix with only fly ash.



Figure 3. Microhydration heat.

3.2. Mortar Flow

Figure 4 shows the flow change in the mortar including ferronickel-slag powder and fly ash. As shown in the figure, the flow of the FA20FN00 mix with 20% of fly ash was approximately 114 mm, whereas the flow of the FA15FN05 mix with 15% of fly ash decreased slightly, resulting in 110 mm. In addition, the flow of the samples containing at least 10% of ferronickel-slag powder approximately ranged from 117 to 124 mm, and the mortar flow increased as the amount of ferronickel-slag powder increased. However, the difference in mortar flow was found to be insignificant.

This implies improved fluidity [11], by the vitreous properties of ferronickel-slag particles, and is similar to the results reported in previous studies [18–20] using ferronickel slag as fine aggregate.

3.3. Compressive Strength

Figure 5 shows the change in compressive strength of mortar mixes including ferronickelslag powder and fly ash. The compressive strength of the FA15FN05 and FA20FN00 mixes including at least 15% of fly ash was relatively high, reaching approximately 35.8 MPa after 7 days. The compressive strength of the FA00FN20 mix including only ferronickel-slag powder without fly ash was the lowest, with a value of approximately 30.7 MPa after 7 days. In addition, the compressive strength of the FA10FN10 and FA05FN15 mixes containing 5 and 10% of fly ash was approximately 3.3 to 4.5% lower than that of the FA20FN00 mix. In case of 28 days of age, the compressive strength of the FA20FN00 mix was approximately 39.6 MPa, that is, higher than that of other samples, whereas the compressive strength of the FA05FN15 mix including 15% of ferronickel-slag powder was 35.0 MPa, which was approximately 11.6% lower than that of the FA20FN00 mix containing only fly ash. Even at the age of 56 days, the FA20FN00 samples, which used 20% fly ash, had the highest compressive strength, reaching approximately 41.9 MPa. This seems to be due to the pozzolanic reaction of fly ash. The compressive strength of the mixes containing ferronickel-slag powder approximately ranged from 38.0 to 39.6 MPa, that is, from 5.4 to 12.0% lower than that of the FA20FN00 sample.



Figure 4. Mortar flow.



Figure 5. Compressive strength.

3.4. Drying Shrinkage

Figure 6 shows the change in the drying shrinkage of mortar according to the replacement ratio of fly ash. The drying shrinkage of the FA20FN00 sample including only fly ash was the highest, reaching approximately 0.148% after 56 days, whereas the FA00FN20 sample without fly ash presented the lowest shrinkage, 0.124%.



Figure 6. Drying shrinkage.

In addition, the drying shrinkage of the FA15FN05, FA10FN10, and FA05FN15 samples containing from 5 to 15% of fly ash was similar, ranging from 0.132 to 0.136%. In general, the drying shrinkage of the samples containing ferronickel-slag powder was slightly lower than that of the samples including fly ash. This is supposed to be due to the contribution of the tight pore structure of the hardened mortar [13] by mixing the ferronickel-slag powder. Therefore, if ferronickel-slag powder is used as a cement substitute, it is likely to be effective in controlling the drying shrinkage of cement mortar and concrete.

3.5. Carbonation Depth

Figure 7 shows the accelerated carbonation depth of cement mortar according to the fly-ash replacement ratio. The carbonation depth of the FA20FN00 and FA15FN05 samples containing more than 15% fly ash ranged approximately from 6.85 to 6.92 mm, that is, larger values than those of the other samples. In addition, the carbonation depth of the FA10FN10 and FA05FN15 samples containing from 5 to 10% of fly ash ranged from 5.18 to 5.31 mm, that is, 22.4 to 25.1% lower than that of the FA20FN00 sample. This seems to be due to the decrease in alkalinity of the cement matrix resulting from the pozzolanic reaction of fly ash in the mixes in which the amount of fly ash is relatively high. The carbonation depth of the sample containing more than 15% of fly ash, but it was higher than the carbonation depth of the FA10FN10 and FA05FN15 samples combining fly ash and ferronickel-slag powder. Therefore, instead of using fly ash or ferronickel-slag powder alone, mixing them is likely to be more effective in increasing the carbonation resistance of the cement mortar.



Figure 7. Accelerated carbonation depth.

4. Conclusions

The following conclusions were drawn from the presented results:

- (1) The difference between the microhydration heat of the three mixes was not large. Note that the microhydration heat of the FA20FN00 mix was slightly higher than that of the FA00FN20 mix. It is supposed that the use of the ferronickel-slag powder can reduce the hydration heat of mortar and concrete. In addition, the flow of the samples containing at least 10% of ferronickel-slag powder ranged approximately from 117 to 124 mm. The mortar flow increased as the amount of ferronickel-slag powder increased.
- (2) The compressive strength of the FA15FN05 and FA20FN00 mixes using more than 15% of fly ash was relatively high, reaching approximately 35.8 MPa after 7 days. After 28 days, the compressive strength of the FA20FN00 mix was approximately 39.6 MPa, that is, higher than that of other samples, and the compressive strength of the FA05FN15 mix using 15% of ferronickel-slag powder was 35.0 MPa, that is, approximately 11.6% lower than the FA20FN00 mix including only fly ash.
- (3) The drying shrinkage of the FA20FN00 sample containing only fly ash was the highest, whereas the FA00FN20 sample without fly ash presented the lowest shrinkage compared to the other mixes. Therefore, if ferronickel-slag powder is used as a cement substitute, it is likely to be effective in controlling the drying shrinkage of cement mortar and concrete.
- (4) The carbonation depths of the FA20FN00 and FA15FN05 samples including more than 15% of fly ash ranged approximately from 6.85 to 6.92 mm, that is, larger than that of the other samples. The carbonation depth of the FA00FN20 sample without fly ash was lower than the carbonation depth of the sample containing more than 15% of fly ash, but it was higher than the carbonation depth of the FA10FN10 and FA05FN15 samples containing both fly ash and ferronickel-slag powder. In general, the carbonation resistance of the sample with FA and FN was better than that of the sample using FA or FN alone.

Further studies are needed to confirm the effects of the chemical components of the materials on the strength and durability of cement mortar and the pozzolanic activity index (PAI), etc.

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