

Physical and Chemical Properties of Nano-slag Mixed Mortar

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Abstract

As buildings have become higher and larger, the use of high performance concrete has increased. With this increase, interest in and use of ultra fine powder admixture is also on the rise. The silica fume and BFS are the admixtures currently being used in Korea. However, silica fume is exclusively import dependent because it is not produced in Korea. In the case of BFS, it greatly improves concrete fluidity and long-term strength. But a problem exists in securing early strength. Furthermore, air-cooled slag is being discarded, buried in landfills, or used as road bed materials because of its low activation energy. Therefore, we investigated in this study the usability of nano-slag (both rapidly-chilled and air-cooled) as an alternative material to the silica fume. We conducted a physic-chemical analysis for the nano-slag powder and performed a mortar test to propose quality standards. The analysis and testing were done to find out the industrial usefulness of the BFS that has been grinded to the nano-level.

Keywords : Nano-slag, Rapidly-chilled Nano-slag, Air-cooled Nano-slag, Flow Value Ratio, Activity Index, Dry Nano Grinding process

1. Introduction

1.1 Background and Purpose of Study

With today's buildings becoming bigger and higher, the use of high performance concrete (HCP) is on the increase because of its strength, water-tightness, and chemical resistance. Furthermore, the importance of admixture as an essential ingredient of HCP concrete is also on the rise. The following are the major admixtures that improve the properties of concrete and make the mortar denser: fly ash, blast-furnace slag (BFS), and silica fume. Silica fume required in the making of ultra-high-strength concrete (over 15,000cm³/g)[1] is a high volume powder that can improve the initial and long-term strength of the concrete and also its chemical durability. However, Korea has been relying solely on imports for the silica fume and there

are various problems including the use of chemical admixtures due to slump reduction. Therefore, the need exists to develop a Korean admixture in place of the silica fume which can increase concrete strength and durability.

On the other hand, the rapidly-chilled BFS powder contributes greatly to the improvement of concrete fluidity and long-term strength. However, reports show that there is a problem in securing early strength. In the case of air-cooled BFS, it falls behind in activation energy compared to the rapidly-chilled BFS and therefore has limits in being used as a concrete admixture. At the same time, it is being used as a low-cost material for road bed material or aggregate and the rest are being either buried in landfills or discarded.

As a solution to these problems, the application of nano-technology to the powders mentioned above is coming to the fore. Nano-powders, if used in the architecture industry, can have properties that the micron powders could not have. As the size of the powder gets smaller, the Surface-Area Effect and the Capillarity Effect [2] will both increase. The powders that have become sized down to the

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nano-level, when used as concrete admixtures, are expected to show superior results.

This study, therefore, probed into the nanomization (dry nano grinding*) of rapidly-chilled and air-cooled BFS which are high in production both in Korea and abroad and can be productized and standardized. The study investigated into the performance and usability of the rapidly-chilled BSF as an alternative material to the silica fume, which is exclusively import dependent in Korea. A new response mechanism for the air-cooled BSF, a low-cost material currently being used as an embankment aggregate or being discarded, was also examined to develop standards for the performance and quality of BSF that have been grinded into nano particles.

1.2 Method and Scope of Study

For the rapidly-chilled slag, we used fineness of over 30,000 cm^2/g and in case of the air-cooled slag, we used fineness of over 90,000 cm^2/g . With the two slags, we analyzed physic-chemical properties and the dynamic properties of the mortar. Then we investigated KS standards and international standards for the admixtures. The scope of this study extends to proposing experimental methods and quality standards for the nano slag that can be the forerunner of international standards.

2. Test Overview

2.1 Test Materials

For the physic-chemical analysis of the nano-sized slag mentioned above, we conducted handling processes appropriate for each analysis method and then performed experimental analysis. We used Joomoonjin standard sand of grading line for the conventional standard experiment of the mortar. For the standard testing, we produced the reference mortar in accordance with KS L ISO 679 - Method of testing cement strength. As the method of the standard testing, we used Joomoonjin standard sand of grading line in comparison with the ISO international standard

sand of grading curve. To minimize error during the making of the testing objects, we used the Jolting Apparatus and compressive strength, Zig - both from the internationally accredited British company E.

Table 1. Chemical Composition and Physical Properties of Cement

Chemical composition	Components	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	lg.loss
	Content (%)		21.95	6.59	2.81	60.12	3.32	2.11
Physical property	Specific surface proportion (cm ² /g)	Setting time			Compression strength (MPa)			
		Initial	Final	3 days	7 days	28 days		
	3,112	3.15	4h	6h	19.8	27.2	38.9	

Table 2. Chemical composition and physical properties of admixtures

Name	Chemical composition					Proportion	
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO		
silica fume	SiO ₂ :94%Norwegian					2.11	
BS1						2.82	
Nano Rapidly chilled	RCNS- I	30.9	13.2	1.04	46.9	6.31	2.86
	RCNS- II						2.84
	RCNS- III						2.84
Nano air-cooled	ACNS- I	50.33	10.27	0.23	37.89	0.82	2.88
	ACNS- II						2.88
	ACNS- III						2.86

Table 3. Grade of standard sand used for testing cement strength (KS L 5100:2006)

Mesh size (mm)	Cumulated dust on mesh (%)
2	0
1.6	7 ± 5
1	33 ± 5
0.5	67 ± 5
0.16	87 ± 5
0.08	99 ± 1

2.1 Physico-chemical analysis

To investigate the performance and changes in property of the rapidly-chilled and air-cooled slag following nanomization, we used Type III BFS. After producing Type I using the conventional grinding method, we proceeded with nanomization. While maintaining equivalence of the specimens, we conducted BET analysis, a fineness measurement method using nitrogen absorption, and SEM, EDS, TEM, and XRD analysis.

2.2 Mortar test method

There are four standards for admixtures in Korea (granulated BFS, BFS aggregate, fly ash, silica fume [5,6,7,8]) and three testing methods for concrete admixtures. But, as it can be seen in Table 4, the mix ratio for performance evaluation is different for each method. Therefore, to test the performance of a new admixture, such as the nano-slag of this study, a new mix ratio is needed.

Consequently, as an integrated solution to evaluating admixtures, we came up with our own testing method in accordance with the "KS L ISO 679: Method of testing cement strength". We proceeded with testing methods and mix ratios in accordance with the use of ISO standard sand. Along with performance comparisons with other admixtures according to their own standards, we also calculated optimum activation levels and flow values for the nano slag. In this manner, we proceeded with the mortar testing for setting the standard testing method for the nano slag. The replacement ratio of each admixture was raised from 10 to 50% by 10% intervals. To secure reliability for the test data, we doubled the number of specimen; six was used as one batch.

3. Test Results

3.1 Physico-chemical analysis results

3.1.1 BET (Brunauer Emmett Teller)

BET measurements of the rapidly-chilled and

air-cooled slag after nanomization (rapidly-chilled nano-slag (RCNS) and air-cooled nano-slag (ACNS)) showed the following results: RCNS - approximately four times the fineness of the conventional Type I BFS (8,000 ~ 10,000 cm^2/g); ACNS - shown in table 7. Considering the low activation level of the ACNS in comparison with the RCNS, it was fine grinded so that the fineness level is two to three times higher than the RCNS. This was done as a measure to increase activation of ACNS and raise its utilization.

3.1.2 SEM (Scanning Electron Microscope)

1) 30,000 cm^2/g RCNS

In the case of RCNS in the 30,000 cm^2/g class, the grain sizes ranged from 500 nm to 1 μm . Rather than showing an even distribution, the sizes were measured to be concentrated around either the biggest or the smallest values. The grain shape is angulated and increase in fluidity is predicted to be small. But in some small grain sizes, we observed the shape to be spherical. Consequently, we expect that nanomization in certain ranges may offset the decrease in fluidity caused by the enhancement of fineness. In addition, as for the shape of the overall grain particles, we observed that the small grains were distributed around the bigger grains. We judge that this is because a top-down approach is used for producing the nano slag and grinding is performed on large-size raw material. However, SEM images alone were not enough to decide whether cohesion exists between the particles.

2) 40,000 cm^2/g RCNS

Analysis of the 40,000 cm^2/g RCNS showed less angulated large-size grain shapes in comparison to the 30,000 cm^2/g RCNS and more particles showing a spherical shape. In addition, each particles were measured to be evenly distributed and the cohesion to be greater than before.

Table 4. Performance and Quality Testing of Each Admixture

Mortar Type	Cement	Specimen	Fine aggregate	Water	
BSF testing (KS F : 2563)	Reference mortar	760g	-	1900g	380 ^{ml}
	Test mortar	380g	380g		
silica fume testing (KS F : 2567)	Reference mortar	500g	-	1375g	242 ^{ml}
	Test mortar	450g	50g		
Proposed standard testing	Reference mortar	450±2	0	1350±5	225±1
	Test mortar	-	10~30% replacement		

Table 5. Regulation on activity index of BSF powder for ASTM C 989 concrete

Type	Aging	Average activity index (%)	Each activity index (%)
Type 80		-	-
Type 100	7 days	Over 75	Over 70
Type 120		Over 95	Over 90
Type 80		Over 75	Over 70
Type 100	28 days	Over 95	Over 90
Type 120		Over 115	Over 110

Table 6. KS F 2563 BSF powder Quality Standard

Type Standard	BFS powder		
	Type 1	Type 2	Type 3
Concentration (g/cm ³)	Over 2.80	Over 2.80	Over 2.80
Specific Surface (cm ² /g)	8,000 ~ 10,000	6,000 ~ 8,000	4,000 ~ 6,000
Activity Index (%)	Aged 7 days Over 95	Over 75	Over 55
	Aged 28 days Over 105	Over 95	Over 75
	Aged 91 days Over 105	Over 105	Over 95
Flow value ratio (%)	Over 95	Over 95	Over 95
MgO (%)	Below 10.0	Below 10.0	Below 10.0
SO ₃ (%)	Below 4.0	Below 4.0	Below 4.0
Ignition loss (%)	Below 3.0	Below 3.0	Below 3.0
Chloride Ion (%)	Below 0.02	Below 0.02	Below 0.02

Table 7. BET Analysis Results

Item Specimen Name	Specific surface (cm ² /g)	
silica fume	220,000	
BS1	11,200	
Rapidly-chilled nano	RCNS-I	36,000
	RCNS-II	39,100
	RCNS-III	44,900
Air-cooled nano	ACNS-I	96,400
	ACNS-II	124,000
	ACNS-III	137,000

This means that the observation shows that as the fineness increases, rather than the number of the biggest particles increasing, the deviation of the particles becomes smaller. In the case of the nano-slag that has such optimum grain size distribution, we judge that not only increase in strength but also increase in fluidity can be expected. However, as for the cohesion state of the particles following increases in attraction and cohesion due to the enhancing of fineness, we had difficulty in deciding on the existence of independent particles by using SEM images only. Therefore, we conducted a Transmission Electron Microscopy (TEM) to observe more precisely the size and shapes of the sand grains.

3) 90,000cm²/g ACNS

BET measurements for the ACNS showed a fineness level two times higher than the RCNS. However, SEM images showed clusters of particles in comparison to the RCNS. This was observed to be a cohesion effect between the particles as the fineness was increased. Therefore, just like the RCNS, the SEM images alone were not enough to know the difference in shapes according the fineness of the nano-slag. We conclude that an alternative testing method to SEM is needed to evaluate the sub-micron particles.

Type		1k	5k	10k
R C NS	30,000 (cm^2/g)			
	40,000 (cm^2/g)			
A C NS	90,000 (cm^2/g)			

Figure 1. SEM images of Nano-slag

3.1.3 EDS (Energy Dispersive Spectroscopy)

1) RCNS (30,000 and 40,000 cm^2/g)

EDS analysis of 30,000 cm^2/g RCNS show similar results to the chemical composition of the conventional BFS; Si ion and Ca ion centered around O ion were the major components. In the case of Mg ion, it was measured to be below 10% – meeting the quality standard of KS F 2563.

EDS analysis of 40,000 cm^2/g RCNS showed that in comparison to the 30,000 cm^2/g RCNS, the maximum peak points for Ca ion and Si ion increased but the peak point for O ion decreased. This seems to be because EDS analysis is a 100 percent conversion ratio rather than a quantitative analysis; as Si and Ca ion were measured to be big the O ion seemed to have relatively decreased. Activity cannot be determined precisely by EDS analysis. However, the nanomization of the same material leads to increase in fineness which subsequently leads to the increase in the peak points of the Ca and Si ion which both affect activity. Therefore, we predict that performance improvement is possible.

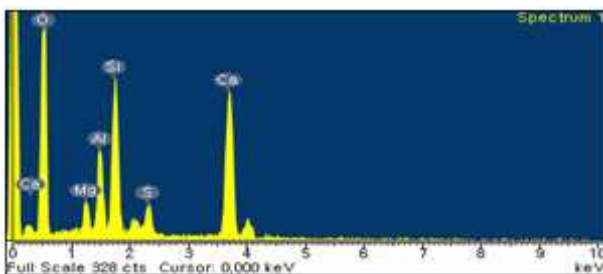


Figure 2. RCNS (30,000 cm^2/g) EDS Analysis Results

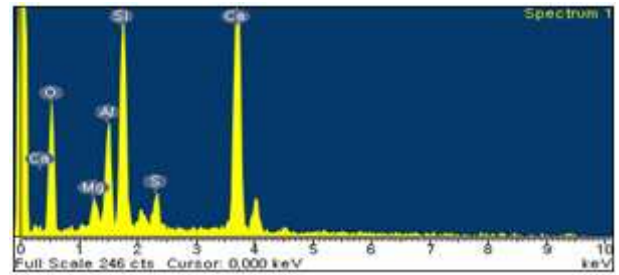


Figure 3. RCNS (40,000 cm^2/g) EDS Analysis Results

2) 90,000 cm^2/g ACNS

ACNS showed equal Ca and Si ion to that of typical air-cooled slag. Considering that air-cooled slag is mostly inactive matter, however, we could not determine from the EDS analysis alone whether each element was active or not. Meanwhile, a Ti mineral ion was measured in the ACNS; it had not shown up in the RCNS. We concluded that this is because as the slag is air-cooled, glassy ions combine with each other to form a crystal and produce an inactive mineral. We predict that the increase of such minerals will lower the activity of the total ACNS while improving hardness.

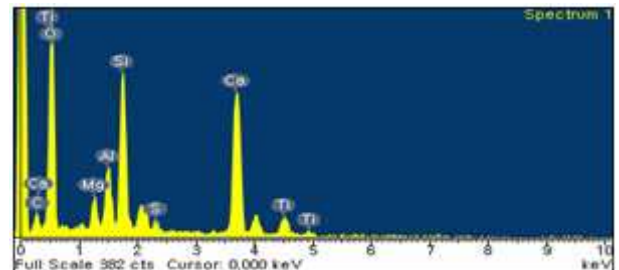


Figure 4. ACNS EDS Analysis Results

3.1.4 TEM (Transmission Electron Microscope)

1) 30,000 cm^2/g RCNS

TEM analysis results showed that the sizes of the particles ranged from 200 nm to 5 μm . Unlike the SEM analysis, we were able to confirm whether each grain existed as an independent particle. Phase analysis of the right crystal structure in Figure 3 shows more than two circles that have a bright light in the center. We were therefore able to confirm that the RCNS is a polycrystalline having several types of ions. We also noticed irregularly distribution of

scatter waves shining brightly as spots around the white center circle was. Generally in the case of crystalline, if the scattered atoms are regularly arranged, then the scattered waves show up strongly in a specific direction. This is not the case for the RCNS; hence, it is an amorphous crystalline.

2) 40,000 cm^2/g RCNS

In the case of the 40,000 cm^2/g RCNS, submicron particle components under 200 nm were observed around the medium-size crystals. In addition, the cohesion state between the particles which could not be distinguished with SEM could be differentiated by looking at the color differences between the crystals. Therefore, a clearer analysis was possible. Furthermore, as the particle sizes got smaller, the shapes showed to be spherical. As seen in Figure 4, in the interior of 100~200 nm size particles, a separate particle with size below 50 nm was observed. Phase analysis according to crystalline structure show irregular scattering of rotational type identical to the 30,000 cm^2/g RCNS. Therefore, it was confirmed to be an amorphous polycrystalline with activity. Consequently, as the fineness increases, the particle shapes can be made into spherical shapes. Even when grinding is not complete, we expect that as active particles are exposed to the outside (contact surface with water during hydration of cement), the performance of the admixture can be improved.

3) 90,000 cm^2/g ACNS

Overall particle sizes were measured to be smaller than the RCNS; fine particles were measured to be cohered around mid-size particles. We see this to be caused by the cohesion effect mentioned above. We were able to confirm through color observation that after grinding, most of the previously clustered nano particles existed independently. In addition, phase analysis based on crystalline structure shows that like the right side in Figure, a regular scattering shape of diffraction ring pattern was observed – something that was not seen previously in the RCNS. Therefore, we observed that ACNS were mostly polycrystalline inactive matter. As the results on the right side in the bottom of the figure show, some irregular scattering were confirmed although it was

not as irregular as the one in RCNS. Therefore, we were also able to confirm that there are matters even in the ACNS that impact hydration.

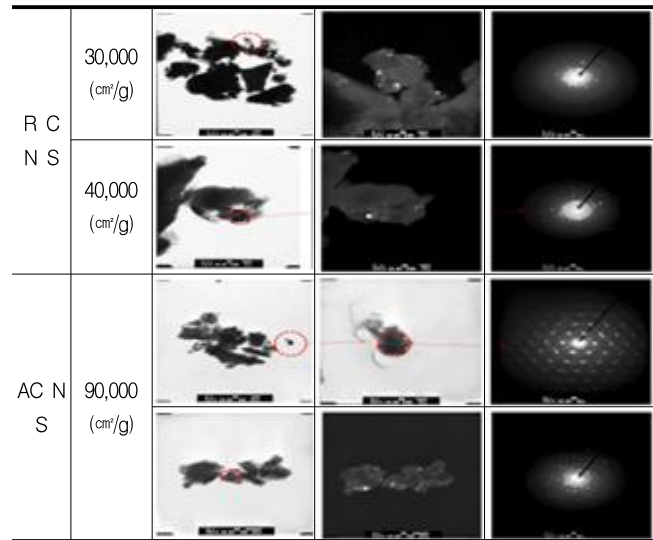
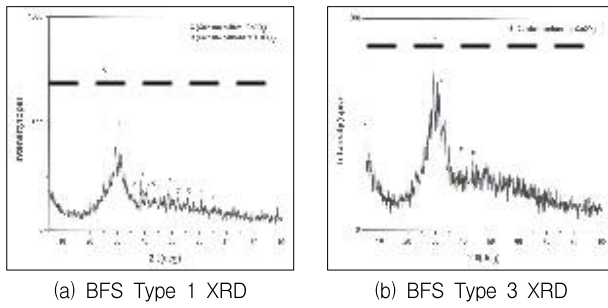


Figure 5. TEM for each Nano-slag type

3.1.5 XRD (X-Ray Diffractometer)

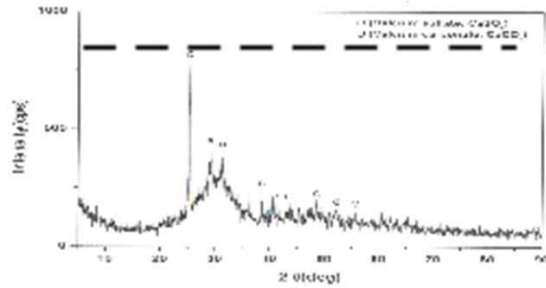
1) RCNS

XRD analysis results of BFS Type 1 and Type 3 showed that as the fineness increases, the maximum peak point rapidly increases to over 500 cps. BFS Type 1 and Type 3 differ greatly not only in their performance and quality but also in cost and size. It is impossible, however, to make the distinction with the naked eye and therefore their maintenance is difficult in construction sites. In the case of XRD though, the distinction can be made in a short time at a low cost. Therefore, we anticipate that the XED will be utilized as an activity improvement index according to fineness and as a performance verification equipment on site. Meanwhile, we measured that the peak point of the RCNS improved to a maximum of 200 cps in comparison to BFS Type 1. More Calcium Sulfate was observed in the RCNS than in the conventional BFS Type 1. In addition, the maximum peak point was measured to be lower in comparison to the silica fume. However, one of the main components of silica fume is SiO_2 (over 99%) which affects long-term strength and BFS is high in calcium content (within 30%) which affects initial hydration. Therefore, we predict that we will be able to secure initial strengths similar or exceeding that of the silica fume.

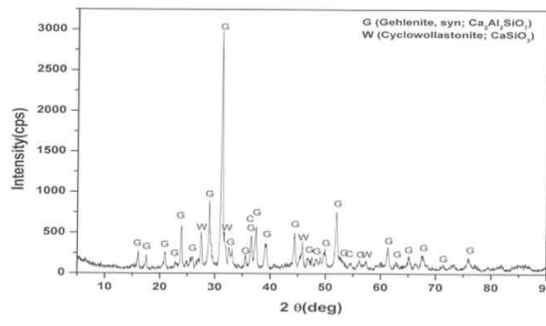


(a) BFS Type 1 XRD

(b) BFS Type 3 XRD



(c) RCNS XRD



(d) ACNS XRD

Figure 6. XRD Analysis Results

2) ACNS

XRD analysis of ACNS showed the presence of Gehlenite and Cyclo wollastonite – both elements that had not been observed in the BFS Type 1, 3 and in the RCNS. We predict this is because in the case of ACNS, as the glassy ion that was melted in the high temperatures of the blast furnace goes through aging, the elements are generated in the process of crystallization due to combination between the ions. The two minerals above are both a kind of Melilite and are of the Melilite compound structure composed of Gehlenite and Cyclo wollastonite. They are matters artificially produced in the slag during refinement of iron ore. The components are minutely different

according to aging periods; however, we conclude that we can expect increase in fluidity, lowering of hydration heat, and resistance to neutralization because of the Sodium thiosulfate ion that is generated during nanomization under moisturized conditions.

3.2 Mortar Test Results

Proposed test method in accordance with KS L ISO 679

1) Fluidity property

Study of the fluid property of the RCNS in accordance with proposed testing method showed that as the replacement ratio increased, the fluidity decreased. However, under conditions that the replacement ratio was below 20%, RCNS showed similar results to OPC. We deem that this is because as we mentioned the basic property of RCNS comes from BFS and in case of BFS, increase in viscosity due to acid coating is small when BFS comes in contact with water. In conditions of over 30%, we conclude that the fluidity reduces in accordance with the increase in replacement ratio of the RCNS with high fineness level.

Study of the fluid property of the ACNS in accordance with replacement ratio showed that in conditions under 30%, as the ratio increased, the fluidity increased linearly. However, when the ratio was over 40%, a rapid decrease in fluidity was observed. We give the following reason for this phenomenon. Just as the results from the physic-chemical analysis show, in the case of ACNS, increase in fluidity due to Sodium thiosulfate ion is possible when ACNS comes in contact with water. However, when a certain point of replacement is exceeded, then the replacement ratio of the ACNS (96,000cm²/g) which has 30 times higher fineness level than cement (3,100cm²/g) increases.

2) Strength properties

After setting the reference mix ratio in accordance with the proposed testing method, we increased the replacement from 10 to 50% at 10% intervals and then measured the compression strength at each interval.

RCNS did not show much difference in strength corresponding to replacement ratio at three days of aging. As the days of aging lengthened, however, strength increase due to higher replacement ratio could be seen clearly. Under 50% replacement ratio of RCNS, we confirmed that the strength increased to a maximum of 150% the strength of OPC.

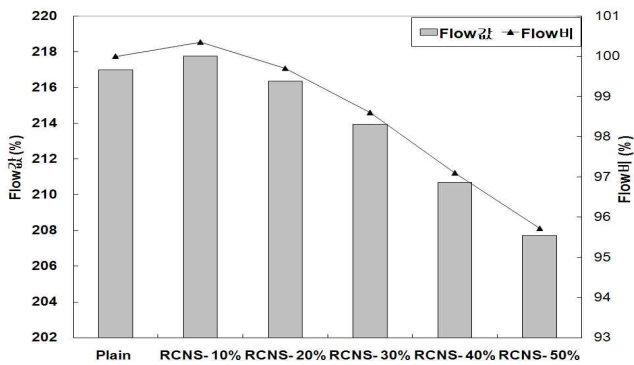


Figure 7. Flow property of RCNS in accordance with KS L ISO 679

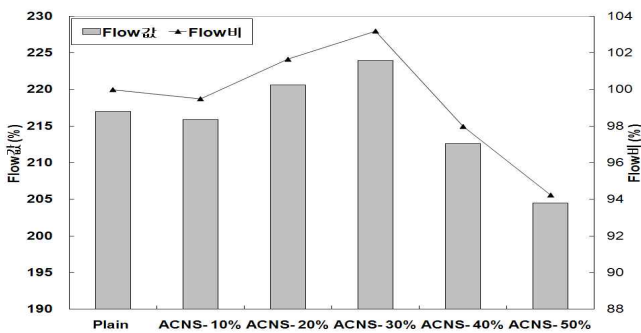


Figure 8. Flow property of ACNS in accordance with KS L ISO 679

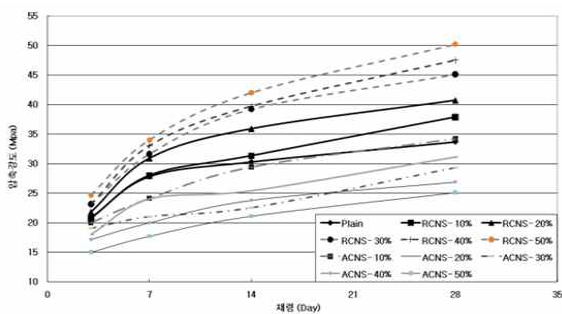


Figure 9. Strength property of different aged nano-slag in accordance with KS L ISO 679

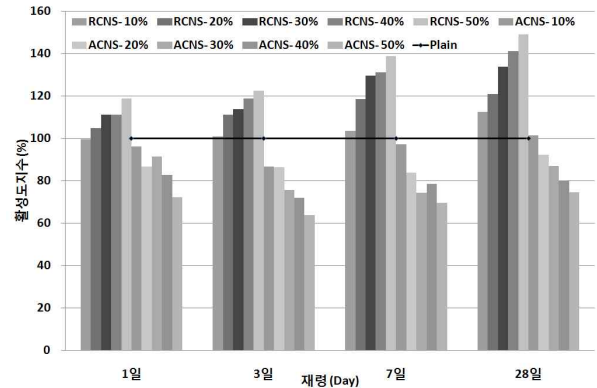


Figure 10. Activity Index of nano-slag in accordance with KS L ISO 679

ACNS showed a decrease in strength as the replacement ratio increased. As the days of aging lengthened, the drop in strength was measured to be bigger. With the replacement ratio at 10%, ACNS showed similar strength properties to OPC. As mentioned previously, this is because below certain replacement ratio levels, strength increase is observed because of the filling effect of micro gaps due to high fineness. But as the replacement ratio of material with low activity increased, the strength was measured to decrease.

3) Activity Index

RCNS showed similar activity index to that of OPC at a replacement ratio of 10% and aging of below 28 days; high strength was confirmed at replacement ratios over 20%. In the case of BFS, increase in strength generally occurs after seven days of aging and the acidic coating has been removed by the concrete alkalinity due to potential hydraulicity. However, RCNS showed over 100% activity index only after 3 days of aging and under all conditionals. RCNS was measured to be superior in improving strength. ACNS showed a decrease in activity as the replacement ratio increased. However, at the replacement ratio of 10%, activity index similar to that of OPC was observed. Furthermore, at aging of 3 days and 28 days, higher activity indexes in comparison to aging of 7 and 14 days, respectively, were measured. In addition, under conditions of ACNS replacement ratios below 40%, ACNS was

found to satisfy the activity standard of BFS Type III (7 days – 55%, 28 days – 75%). When replacement ratio was at 10%, ACNS satisfied the activity standard of BFS Type II.

5. Conclusion

To set up performance and quality indexes for the nano-slag, we conducted a physic-chemical analysis on the RCNS and ACNS produced by dry grinding processes. We also measured fluidity property and activity indexes in accordance with conventional and proposed testing regulations of mortar. The results are as follows.

- 1) SEM analysis showed overall particle sizes ranging from 500 nm to over 1 μm . As the fineness increased, the deviations decreased. We conclude that for measuring fineness of nano-slag, BET will yield a more precise measurement since it tests fineness according to nitrogen absorption. In addition, EDS analysis showed that as the fineness of the nano-slag increased, RCNS showed increases in quantities of Ca and Si ions – both metallic ions.
- 2) TEM analysis showed superiority to the SEM analysis in observing particles. Even for ACNS with its low activity response, we were able to confirm that it is an amorphous polycrystalline with possible activity responses. In addition, XRD analysis showed that RCNS in comparison to general BFS had an increase in the maximum peak point. A Melelite structure which facilitates melting of sulfate ion was observed in the ACNS; therefore, we conclude that performance improvement of slag due to nanomization is possible. We also deem that XRD as an analysis method of high volume powder can be used to distinguish types of BFS and evaluate performance of the nano-slag.
- 3) Testing the dynamic properties of nano-slag in accordance with the proposed testing method (KS L ISO 679) showed a clear change in

fluidity property corresponding to replacement ratio. We conclude that this is because of the use of international standard sand with grading curves and the reduction of granules in comparison to conventional testing methods. Therefore, we suggest that the proposed testing method is more advantageous than the conventional method in observing fluidity. In addition, RCNS showed maximum strength improvement within 50% for the activity index; ACNS showed strength decrease within maximum of 35%. This measurement was similar to the strength property with concrete using general BFS. We conclude that this is because the ratio of granules to aggregates was increased to 1:3 in comparison to the conventional testing method and this ratio is similar to the concrete composition ratio. Therefore, we suggest that the proposed testing method is more advantageous than the conventional method in predicting concrete strength.

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