

## Effect of nano type and slag replacement level on cement mortars

*Nano tipi ve granüle yüksek fırın cürufu ikame oranının çimento harçlarına olan etkisi*

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### Abstract

In the current experimental study, fresh and hardened properties of high-volume ground granulated blast furnace slag blended cements were investigated. For this purpose, fifty-eight cement mortars satisfying minimum requirements of TS EN 197-1 were produced and nano calcite, nano SiO<sub>2</sub> and nano Al<sub>2</sub>O<sub>3</sub> were replaced by the cement up to a replacement level of 4% (which were 1%, 2%, 3% and 4%). First of all, the mechanical properties of mixtures were examined at the curing ages of 2, 7 and 28 days and then standard consistency and setting times of eight selected mixtures were determined. Test results showed that increase in the replacement level of slag was resulted in decrease in early age compressive strength. As a result of both seeding (nucleation) and chemical effect, decrease in setting time and enhancement in early age strength development of mixtures including nanomaterials were observed. Even though increase in replacement of nanomaterials resulted in a slight decrease in compressive strength of the mixtures, the best enhancements were obtained with the replacement level of 1%. As a result of this, minimum requirements of CEM III-C 32.5 were achieved in the mortars including CEM III-C type cement with a slag replacement level of 81% and modified by 1% of nanomaterial.

**Keywords:** Cement mortar, Compressive strength, Ground granulated blast furnace slag, Nanomaterial, Setting time

### Öz

Mevcut deneysel çalışmada, yüksek hacimde granüle yüksek fırın cürufu içeren harçların taze ve sertleşmiş özellikleri incelenmiştir. Bu amaçla, TS EN 197-1'e göre minimum şartları sağlayan ve %1, %2, %3 ve %4 ikame oranlarında nano kalsit, nano SiO<sub>2</sub> ve nano Al<sub>2</sub>O<sub>3</sub> ihtiva eden toplamda 58 karışım tasarlanmıştır. İlk olarak tüm karışımların 2, 7 ve 28. Günlerde mekanik özellikleri incelenmiş, daha sonra seçilen 8 karışım ile harmanlanmış çimento pastaları hazırlanarak standart kıvam suyu ve priz süreleri tespit edilmiştir. Test sonuçları, yüksek hacimlerde granüle yüksek fırın cürufu kullanımının erken yaş dayanım düşüşü ile neticelendiğini göstermiştir. Çekirdeklenme ve kimyasal etkinin bir sonucu olarak nano malzemelerin kullanıldığı karışımların priz sürelerinde kısalma ve erken yaş basınç dayanımı gelişimlerinde iyileşme gözlemlenmiştir. Nano malzeme ikame oranı artıkça basınç dayanımlarında kısmî de olsa bir düşüş gözlemlenirken dayanım gelişimine en yüksek katkının %1-2 arası ikame oranlarında gözlemlendiği tespit edilmiştir. Nano SiO<sub>2</sub>, Nano Al<sub>2</sub>O<sub>3</sub> ve nano kalsit kullanımıyla hem çekirdeklenme hem de kimyasal etkinin bir netice olarak harçların performans özelliklerinde belirgin iyileşmeler saptanmıştır. %81 oranında granüle yüksek fırın cürufunun ikame edildiği CEM III-C tipli katkıli çimentolarda tüm nano tipleri için %1 nano malzeme kullanımıyla CEM III-C 32.5 elde edilmiştir.

**Anahtar kelimeler:** Çimento harcı, Basınç dayanımı, Yüksek fırın cürufu, Nano malzeme, Priz süresi

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## 1. Introduction

In addition to the high energy consumption (Rashad, 2014) in the production of ordinary Portland cement used as a binder in concrete, approximately one cubic meter of carbon dioxide gas is released into the atmosphere in each ton of clinker production, thus cement is globally responsible for about 7% of the annual CO<sub>2</sub> emission (Benhelal et al., 2013; Li et al., 2013). Therefore, since the carbon footprint of cement is very high, the most effective approach to reduce these ecological harmful effects of cement is to partially replace the cement with industrial by-products such as blast furnace slag, fly ash and silica fume (Shaikh and Hosan, 2019; Rashad 2015). Although the use of fly ash and blast furnace slag in high volume has improved workability and long-term mechanical and durability properties and also decrease in heat of hydration, the pozzolanic reactions with calcium hydroxide from cement hydration are very slow and thus early-age mechanical and durability properties are much lower quality than that of normal concrete (Elchalakani et al., 2014; Demirboga et al., 2004).

Due to both amorphous and high hydraulic cementing property, Blast Furnace Slag (S) has been used as a binding material in the cement industry for many years (Ozbay et al., 2016; Kumar et al., 2008). Flower and Sanjayan (Flower and Sanjayan, 2007) showed that a 22% reduction in CO<sub>2</sub> emission would be achieved as a result of 40% replacement of cement by slag for conventional concrete. In addition, the use of moderate replacement levels of slag has a positive effect on both the strength and durability properties of concrete (Bakharey, 2005; Rowles and O'connor 2003). Although slag replacement level could be tailored up to 95% according to TS EN 197-1 (TS EN 197-1, 2012), it cannot be used at high rates in slag blended types of cement due to its low heat of hydration and low early-age strength development (Zhao et al., 2020-a; Zhuang and Wang, 2021). It was suggested by Li et al. (Li et al., 2015) that the rate of slag usage in cement-based materials should not exceed 30%. Oner and Akyuz (Oner and Akyuz, 2007) revealed that the strength development of concrete is restricted if the slag replacement level exceeds 55%.

Recently, the use of nanomaterials in cement-based materials has become the most interesting research area (Zhao et al., 2020-b; Liu et al., 2020; Wu et al., 2020), and although many studies have been carried out so far, experimental studies are still ongoing in this area. Among all nanomaterials,

nano silica (NSI), nano CaCO<sub>3</sub> (NCC) and nano alumina (NA) are used more widely because they improve both mechanical and microstructural properties of cement-based composites (Abhilash et al., 2021; Orakzai, 2021; Poudyal et al., 2021). Since they have a very high surface area to volume ratio, they significantly affect the hydration properties of cement. Depending of the type of nanomaterial being used, they exhibit different effects in cement chemistry and these effects can be categorized under three headings: (i) nucleation effect, (ii) chemical effect, and (iii) dilution effect (Wang et al., 2018; Cao et al., 2019). These effects vary in accordance with nano type, clinker usage rate, mineral admixture type and/or nanomaterial usage rate. For example; the chemical effect is more pronounced in the use of NCC while the nucleation effect is more effective in the presence of NS and NA (Ciftci, 2020). Moreover, this was resulted in selecting an appropriate type of nanomaterials in the presence of the different type and replacement level of mineral admixtures.

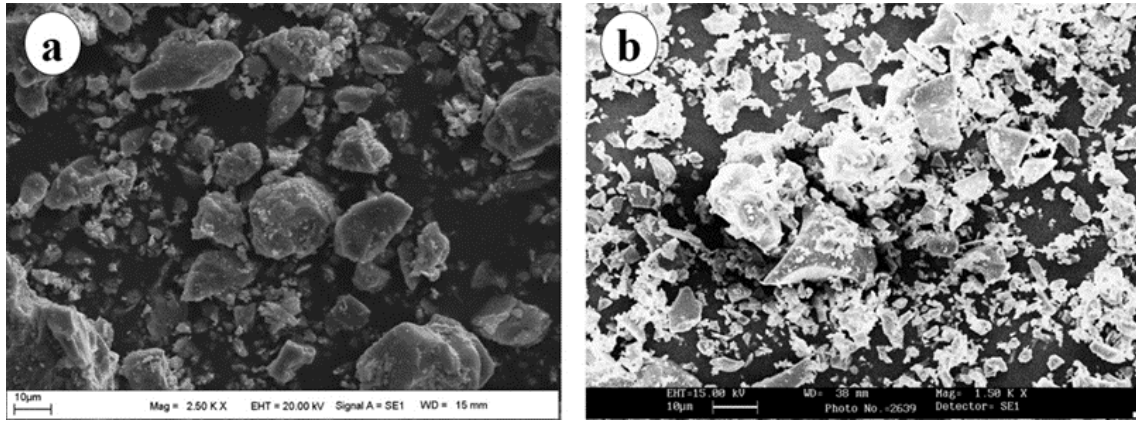
The main purpose of the current experimental study is to produce an eco-friendly cement type in which different nanomaterials and ground granulated blast furnace slag were replaced by cement up to 4% and 81%, respectively. For this aim, S, NS, NA and NC have been used in the tailored mixtures in order to develop properties of high-volume blast furnace slag blended types of cement (including the different amounts of slag) satisfying minimum requirements of TS EN 197-1. Both fresh (consistency and setting times) and hardened properties (compressive strength) of the mixtures containing NS, NA and NC and varying rates of slag (up to replacement level of %81) were examined. For this purpose, 58 mixtures have been prepared in accordance with TS EN 197-1 and then the compressive strength of these mixtures for curing ages of 2, 7 and 28 days has been determined. In addition, 8 mixtures from 58 tailored mixtures were selected and then consistency, initial and final setting times were determined according to TS EN 196-3 (TS EN 196-3, 2017).

## 2. Material method

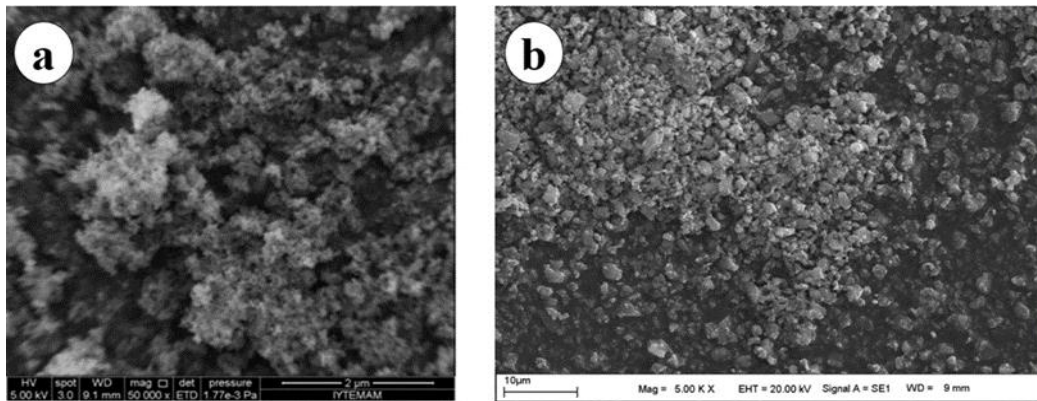
Ordinary Portland Cement (OPC) CEM I 42.5 (which was produced at the laboratory by grinding the clinker and 5% gypsum up to enough fineness) satisfying minimum requirements of TS EN 197-1 was used in the production of cement mortars while ground granulated blast furnace slag (S) whose specific gravity of the slag was 3.21 g/cm<sup>3</sup> and the Blaine specific surface was 4250 cm<sup>2</sup>/g was

preferred as mineral admixture. In addition, commercially available NSI, NA and NC. Standard CEN Reference Sand with a maximum grain size of 2 mm satisfying requirements of TS EN 196-1 (TS EN 196-1, 2016) and tap water were used. Both physical properties and chemical compositions of binders and nanomaterials are given in Table 1. SEM images of OPC, S, NS and NC are given in

Figure 1 (OPC and S) and Figure 2 (NS and NC), respectively. In the current experimental study, a high-water-reducing chemical admixture (HWRA) of Glenium 51 produced by SIKA Construction Chemicals was used. The specific gravity of HWRA, which is a chemical additive in liquid form, is approximately 1.05 g/cm<sup>3</sup>.



**Figure 1.** SEM images of binders (a) OPC and (b) S (Demirhan, 2017)



**Figure 2.** SEM images of (a) NS and (b) NC

**Table 1.** Chemical composition and physical properties of Binders and Nanomaterials

Chemical Composition (%)	OPC	S	NC	NS	NA
CaO	61.36	37.43	56.01	1.10	0.00
SiO <sub>2</sub>	20.41	39.62	0.63	86.99	0.10
Al <sub>2</sub> O <sub>3</sub>	5.34	10.62	0.13	1.19	98.48
Fe <sub>2</sub> O <sub>3</sub>	3.10	1.40	0.22	0.53	0.43
MgO	3.48	6.11	0.54	0.11	0.54
SO <sub>3</sub>	2.57	0.79	0.04	0.21	0.06
Na <sub>2</sub> O	0.37	0.27	0.03	0.66	0.04
K <sub>2</sub> O	0.94	0.96	0.01	0.01	0.00
Loss of Ignition	2.15	2.80	42.39	9.20	0.35
<b>Physical Property</b>					
Specific gravity, g/cm <sup>3</sup>	3.24	2.9	-	-	-
Blaine Surface Area, cm <sup>2</sup> /g	3092	4250	-	-	-
BET surface area, cm <sup>2</sup> /g	-	-	74	1623	325

In total, 58 different cement mortar mixtures including different amounts of slag and nano sized

materials were cast for the experimental study. Water/Binder (w/b) was kept constant as 0.5 since

it is standard in accordance with TS EN 197-1 for all cement mortars. The standard mixture proportions of the 58 mixtures are given in Tables 2-5. All mortars are showed with notation including both letters and numbers which indicate percentage of ingredients. For instance, in the ninth mixture, which is designated as CEM III-B\_NSI\_3 means that cement type is CEM III-B including NSI where it was used at a replacement level of 3. All of the 58 cement mortars were prepared in accordance with the procedure given in TS EN 197-1 standard where total binder (cement and/or slag and/or nano) of 450 g and CEN reference sand of 1350 g and water of 225 g were mixed and standard mortars were cast. All were tested for compressive strength test at the curing ages of 2, 7 and 28 days. Since the main purpose of the current study is to monitor and investigate the developments in the early age properties of cement mortars, only curing ages up to 28 days were taken

into consideration. In addition, before fresh mortars were poured into the standard molds (40x40x160 mm) standard test method for flow of hydraulic cement mortar described in ASTM C1437 (2015) was applied to fresh mortars and slump flows diameters were determined. For the determination setting times as a fresh property, only 8 mixtures given in Table 6 were selected from 58 mixtures since lots of mixtures were included high volume of slag up to 81% of total binder which would result in higher setting times (Zhuang and Wang, 2021). The testing procedure of setting times was conducted according to TS EN 196-3. Therefore, in order to determine the fresh properties of the prepared blends, standard consistency, initial and final setting times were determined for 8 blends selected from 58 blends. 58 blends, produced in terms of hardened properties, were subjected to compressive strength test at the curing ages of 2, 7 and 28 days.

**Table 2.** Mixture proportions of CEM I including different nanomaterial types

Mix #	Mix ID	Cement Type	Binder, %		Nanomaterial, %			HRWA, %	Flow, cm
			OPC	S	NC	NSI	NA		
1	CEM I	CEM I	100	0	0			0	16.5
2	CEM I_NC_1		99	0	1	0	0	0	19.5
3	CEM I_NC_2		98	0	2	0	0	0	18.7
4	CEM I_NC_3		97	0	3	0	0	0	18.8
5	CEM I_NC_4		96	0	4	0	0	0	17.2
6	CEM I_NAL_1		99	0	0	0	1	0.40	17.5
7	CEM I_NAL_2		98	0	0	0	2	0.45	17.6
8	CEM I_NAL_3		97	0	0	0	3	0.50	16.6
9	CEM I_NAL_4		96	0	0	0	4	0.55	16.5
10	CEM I_NSI_1		99	0	0	1	0	0.40	17
11	CEM I_NSI_2		98	0	0	2	0	0.57	16.2
12	CEM I_NSI_3		97	0	0	3	0	1.11	16
13	CEM I_NSI_4		96	0	0	4	0	1.78	17.5

**Table 3.** Mixture proportions of CEM III-A, B and C including NC

Mix #	Mix ID	Cement Type	Binder, %		Nano Type, %	HRWA, %	Flow, cm
			OPC	S	NC		
14	CEM III-A	CEM III-A	64	36	0	0	19.5
15	CEM III-A_NC_1		63	36	1		19.8
16	CEM III-A_NC_2		62	36	2		20.1
17	CEM III-A_NC_3		61	36	3		20.3
18	CEM III-A_NC_4		60	36	4		20.2
19	CEM III-B	CEM III-B	34	66	0		18.5
20	CEM III-B_NC_1		33	66	1		18.7
21	CEM III-B_NC_2		32	66	2		18.7
22	CEM III-B_NC_3		31	66	3		18.9
23	CEM III-B_NC_4		30	66	4		19
24	CEM III-C	CEM III-C	19	81	0		18
25	CEM III-C_NC_1		18	81	1		18.4
26	CEM III-C_NC_2		17	81	2		18.5
27	CEM III-C_NC_3		16	81	3	18.8	
28	CEM III-C_NC_4		15	81	4	19.1	

**Table 4.** Mixture proportions of CEM III-A, B and C including NA

Mix #	Mix ID	Cement Type	Binder, %		Nano Type, %	HRWA, %	Flow, cm
			OPC	S	NA		
29	CEM III-A	CEM III-A	64	36	0	0	19.5
30	CEM III-A_NAL_1		63	36	1	0	19.5
31	CEM III-A_NAL_2		62	36	2	0	19.3
32	CEM III-A_NAL_3		61	36	3	0	18.2
33	CEM III-A_NAL_4		60	36	4	0.04	17.9
34	CEM III-B	CEM III-B	34	66	0	0	18.5
35	CEM III-B_NAL_1		33	66	1	0	18.5
36	CEM III-B_NAL_2		32	66	2	0	18
37	CEM III-B_NAL_3		31	66	3	0	17.2
38	CEM III-B_NAL_4		30	66	4	0	16.7
39	CEM III-C	CEM III-C	19	81	0	0	18
40	CEM III-C_NAL_1		18	81	1	0	17.4
41	CEM III-C_NAL_2		17	81	2	0	17
42	CEM III-C_NAL_3		16	81	3	0.04	16.3
43	CEM III-C_NAL_4		15	81	4	0.13	17

**Table 5.** Mixture proportions of CEM III-A, B and C including NS

Mix #	Mix ID	Cement Type	Binder, %		Nano Type, %	HRWA, %	Flow, cm
			OPC	S	NSI		
44	CEM III-A	CEM III-A	64	36	0	0.00	19.5
45	CEM III-A_NSI_1		63	36	1	0.00	18
46	CEM III-A_NSI_2		62	36	2	0.11	17.7
47	CEM III-A_NSI_3		61	36	3	0.42	17.8
48	CEM III-A_NSI_4		60	36	4	0.82	18.1
49	CEM III-B	CEM III-B	34	66	0	0.00	18.5
50	CEM III-B_NSI_1		33	66	1	0.00	17.5
51	CEM III-B_NSI_2		32	66	2	0.18	16.7
52	CEM III-B_NSI_3		31	66	3	0.56	16.8
53	CEM III-B_NSI_4		30	66	4	1.11	16.7
54	CEM III-C	CEM III-C	19	81	0	0.00	18
55	CEM III-C_NSI_1		18	81	1	0.00	16.7
56	CEM III-C_NSI_2		17	81	2	0.33	16.3
57	CEM III-C_NSI_3		16	81	3	0.71	16.3
58	CEM III-C_NSI_4		15	81	4	1.29	16.7

**Table 6.** Mixture proportions of mixtures chosen for consistency and setting times

Mix #	Mix ID	Cement Type	Binder, %		Nanomaterial, %		
			OPC	S	NC	NS	NA
1	CEM I	CEM I	100	0	0		
2	CEM I_NC_1		99	0	1	0	0
6	CEM I_NAL_1		99	0	0	0	1
10	CEM I_NSI_1		99	0	0	1	0
14	CEM III-A	CEM III	64	36	0		
15	CEM III-A_NC_1		63	36	1	0	0
30	CEM III-A_NAL_1		63	36	0	0	1
45	CEM III-A_NSI_1		63	36	0	1	0

### 3. The research findings and discussion

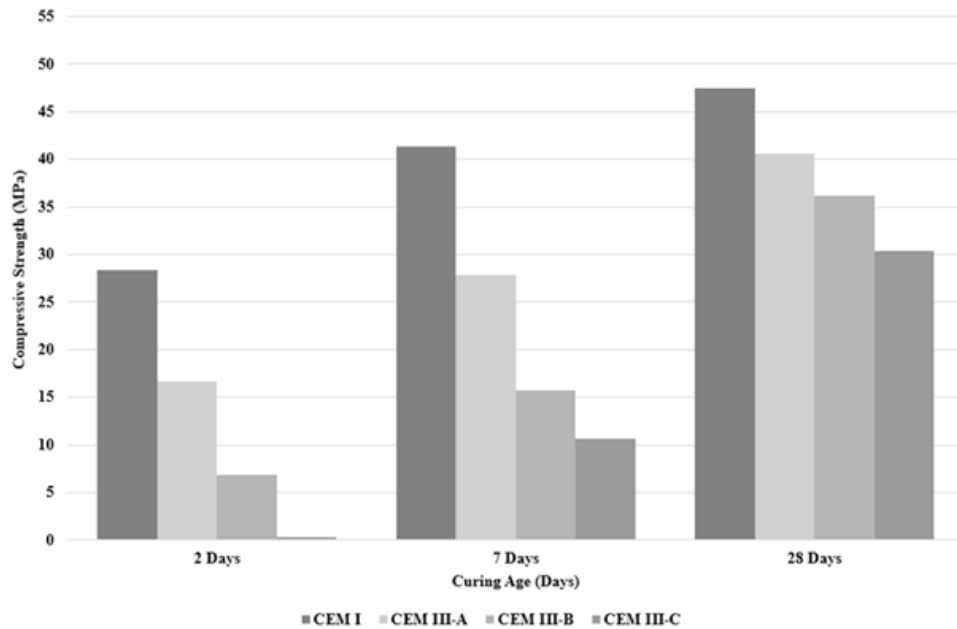
#### 3.1. Compressive strength

In order to avoid confusion as many parameters were examined within the scope of the current experimental study, this section will be discussed under the titles: (i) The effect of slag replacement level, (ii) Effect of nanomaterial type and (iii) Effect of nanomaterial replacement level.

##### i. The effect of slag replacement level

Within the scope of the present study, of the determined 58 blends, slag replacement levels for each blend group were 0% (for CEM I), 36% (for CEM III-A), 66% (for CEM III-B) and 81% (for CEM III-C). Compressive strength test results of

cement mortars for curing ages of 2, 7 and 28 days are given in Figure 3. As seen in Figure 3, as the replacement level of slag increased, a decrease/reduction was observed in both early and later age strength developments. Although slag has a partial hydraulic binding property, its pozzolanic property is more effective.  $F_{CEM\ III-A}/F_{CEM\ I}$ ,  $F_{CEM\ III-B}/F_{CEM\ I}$  and  $F_{CEM\ III-C}/F_{CEM\ I}$  ratios were obtained as 0.85, 0.76 and 0.64, respectively, according to the standard compressive strength of 28 days. This shows that as slag replacement level increased, a significant decrease was observed in the development of early age strength (2-day). This is because of (i) relatively lower cement utilization rates resulted in lower hydration products and (ii) pozzolanic reactivity occurred after hydration reactions.

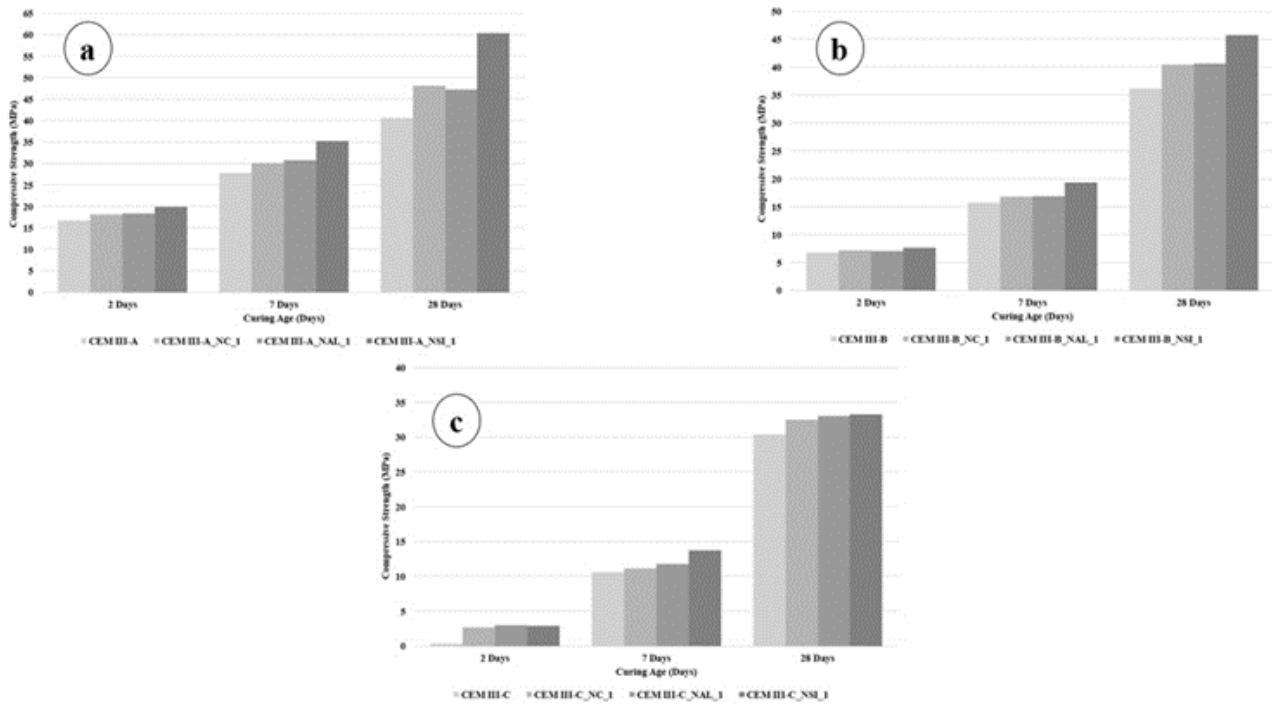


**Figure 3.** Compressive strength results depending on slag replacement level

##### ii. Effect of nanomaterial type

In mixtures containing slag, 2, 7 and 28 days compressive strength test results showed differences in accordance with both nano type and slag replacement level. Compressive strength of mixtures including 1% nanomaterial and different amounts of slag is given in Figure 4. As seen in the Figure, even though 2-day compressive strength of all mixtures are almost the same and closed to each other regardless of nano type, for later ages, the highest strength development of 48.8% was found in the mixture including NSI (Qing et al., 2007; Bai et al., 2014). The contribution of NAL and NSI to the strength development was limited since the amount of calcium hydroxide formed in the hydration decreased due to the reduction in cement

usage. As a result of chemical effect of NC with aluminate phase of both slag and CEM I (Demirhan, 2020), more contributions were obtained in the presence of nano sized calcite (Sato and Daillo, 2010), and even the rate of contribution in many cure ages was almost equal to NAL. Regardless of the slag usage rate, all nanomaterials contributed to the development of strength, and CEM III-C 32.5 N type cement was produced in the standard mixture including 19% cement, namely, 81% of slag usage. Considering the fact that approximately one cubic meter of  $CO_2$  gas is released into the nature when a ton of clinker is produced, makes it possible to produce an eco-friendly greener cement in the case of using 81% of slag.

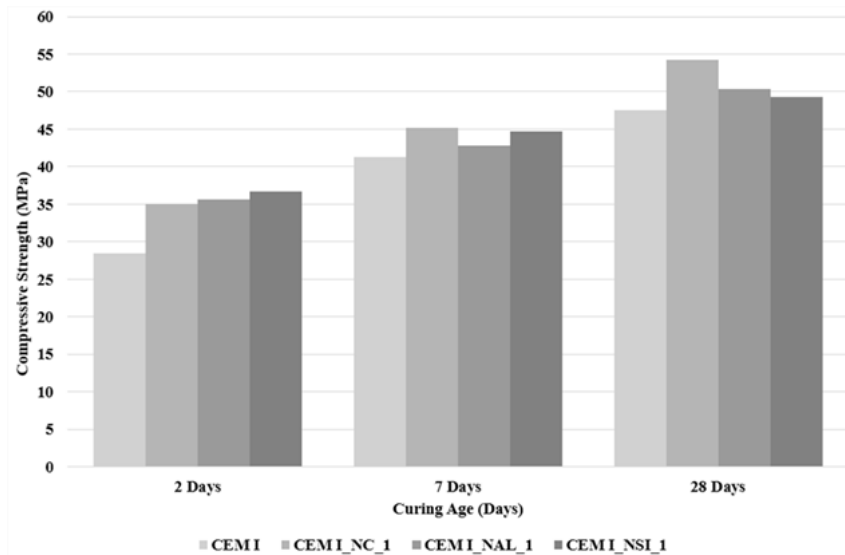


**Figure 4.** Compressive strength results of mixtures including different amount of slag and 1% of nanomaterial (a) for CEM III-A, (b) for CEM III-B and (c) for CEM III-C

In addition to all mentioned above, since there was a little amount of aluminate phase in slag (10.62%, see Table 1), contribution of slag to the strength development in term of chemical effect was limited, therefore, less strength development in higher replacement levels of slag was observed. Since there is more aluminate phase in F type fly ash than that of slag, chemical effect and contribution to strength is at higher levels in the presence of fly ash. Therefore, lower aluminate phase in slag was resulted in lower contribution of NC to the amount of hydration products (Shaikh and Hosan, 2019).

In mixtures without slag, herein also, compressive strength of 2, 7 and 28 days curing ages were varied in accordance with nano type. Compressive strength test results of mixtures with 1% of nanomaterial and also without slag are given in

Figure 5. Regardless of nano type, compressive strength of the mixtures without slag improved in the presence of nanomaterials. Since NAL and NSI promote the hydration kinetics of  $C_3S$  (Björnström et al., 2004; Barbhuiya et al., 2014) and therefore higher amount of calcium hydroxide forms, the highest strength development was observed at the curing age of 2 days where enhancement of %25.4 and %29.2 comparing to control mixture (Mix# 1) were obtained in the presence of NAL and NSI, respectively. In the presence of NC, in addition to promoting hydration mechanism of  $C_3S$ , NC reacted with aluminate phase of OPC and produced hydration products of carbo-aluminates (Zaitri et al., 2014; Dale et al., 2015). As a result of this, the highest strength enhancement at the curing age of 28 days was observed in the presence of NC with an enhancement of 14%.

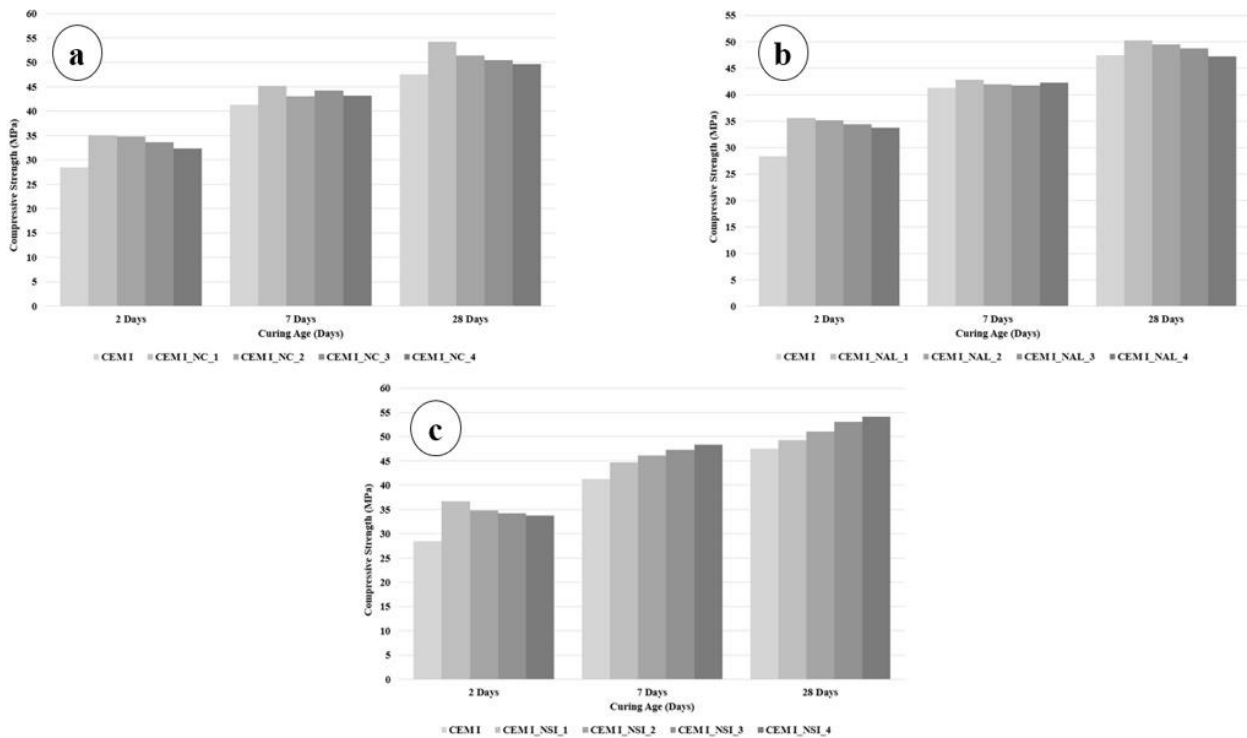


**Figure 5.** 2, 7 and 28 days compressive strength results of mixtures including 1% of nanomaterial without slag

*iii. Effect of nanomaterial replacement level*

Compressive strength test results of mixtures including different amounts of nano are given in Figure 6-9. As seen in the figures, regardless of slag replacement level, a partial decrease in the compressive strength was observed as nanomaterial usage percentage was increased. Decrease in the strength was maybe due to both the agglomeration of nanomaterials and also dilution effect. Since nanomaterials have high surface area

to volume ratio, especially when they are used over a certain ratio, they act as a filler and do not contribute to strength (Sun et al., 2020; Ng et al., 2020). Although nanomaterial replacement level varies in the literature, in many studies, the rate of nano usage is recommended between 1-2% (Yang et al., 2018; Shaikh and Supit, 2014), and in the current study, the highest strength development was observed in the 1% use of nanomaterials where the result is in line with the literature.



**Figure 6.** 2, 7 and 28 days compressive strength results of mixtures including different amount of nanomaterial without slag



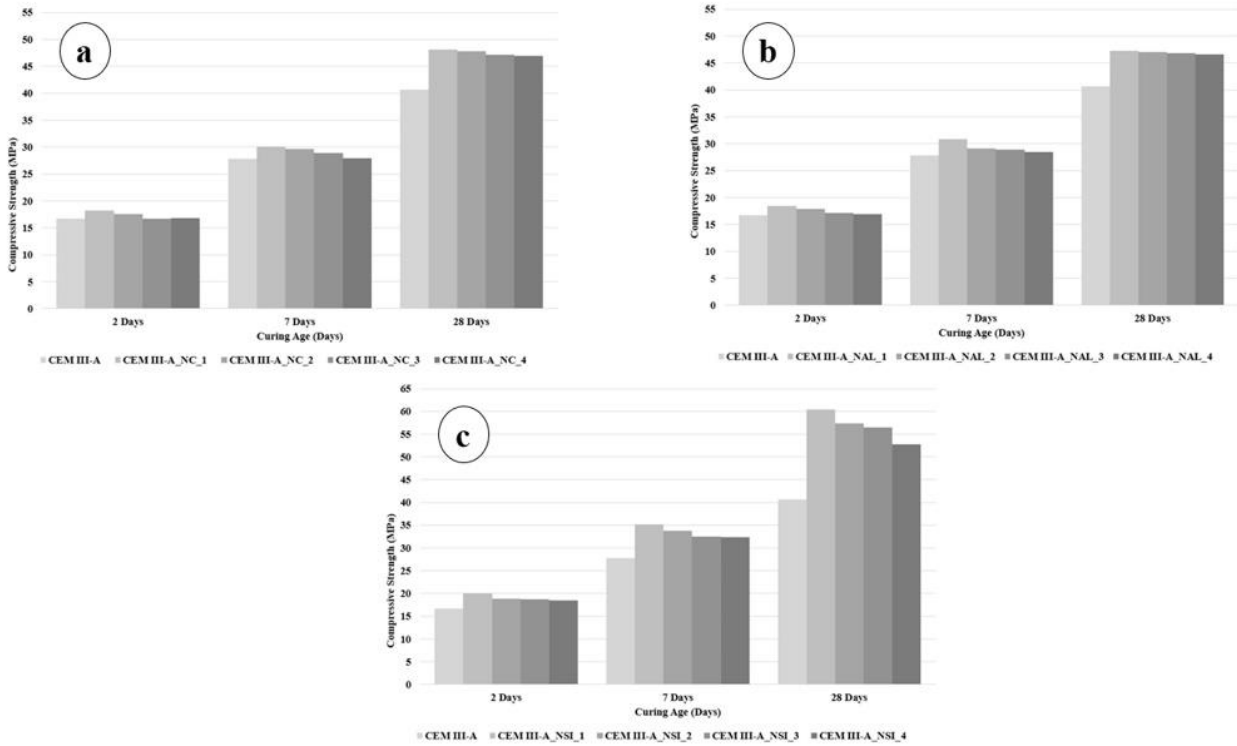


Figure 7. Compressive strength results of mixtures for CEM III-A including different amount of nanomaterial

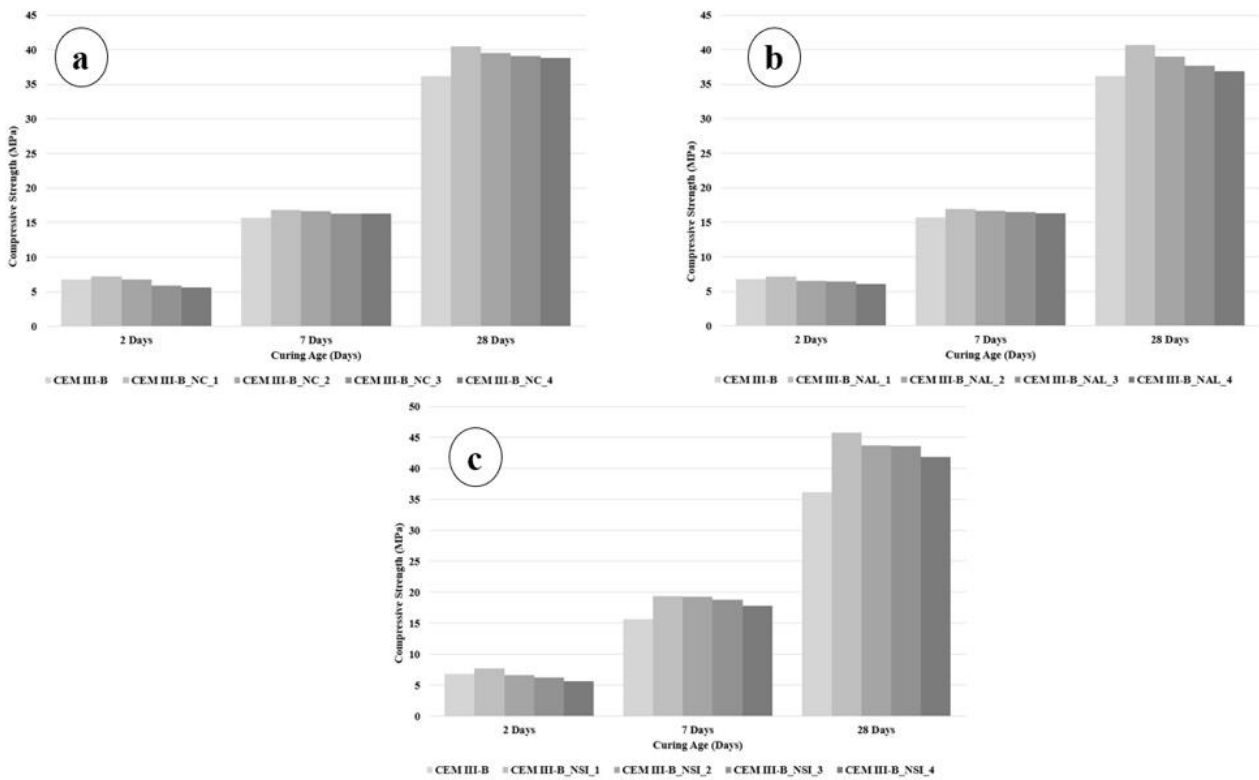
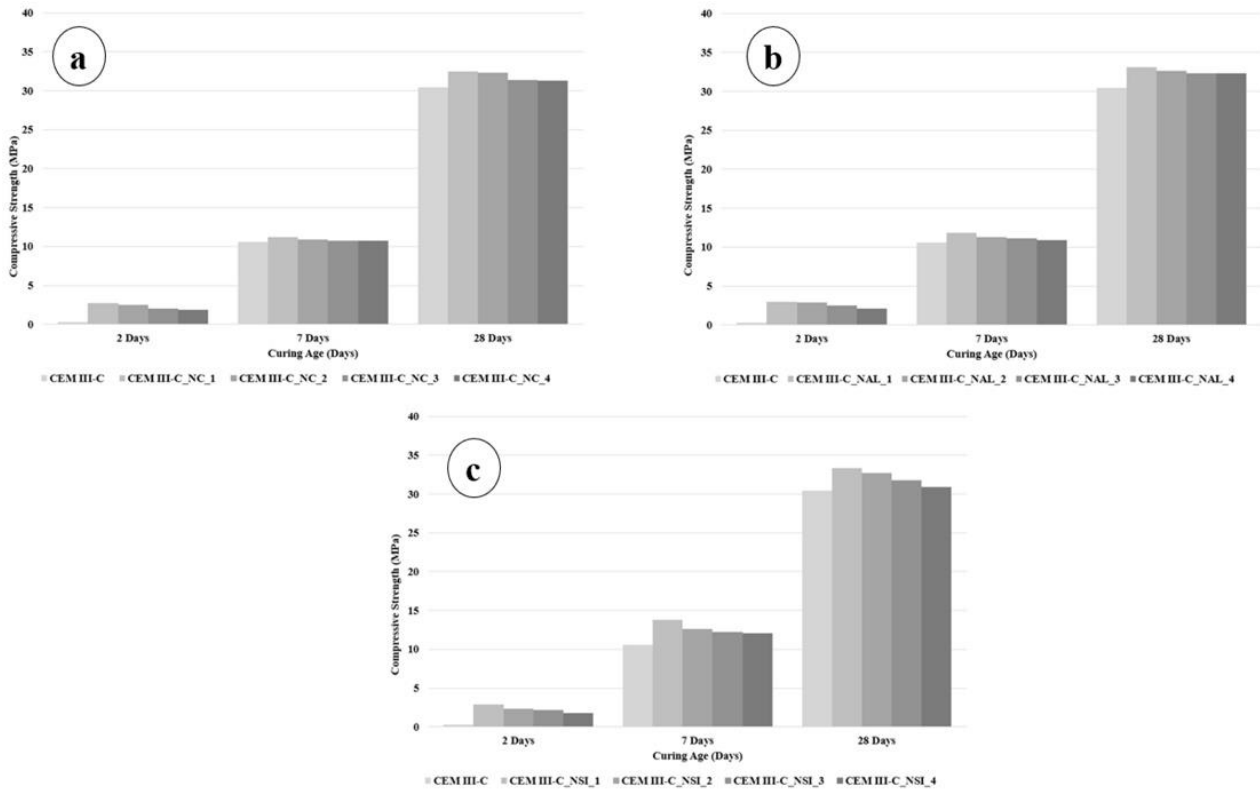


Figure 8. Compressive strength results of mixtures for CEM III-B including different amount of nanomaterial

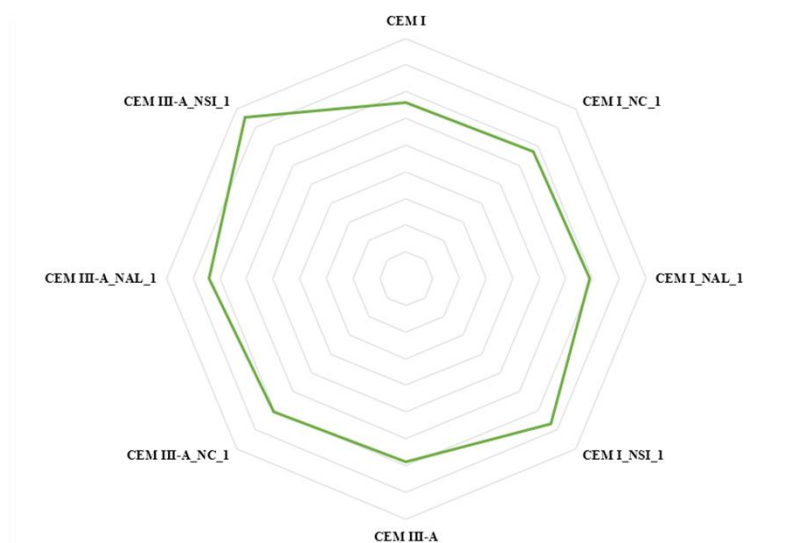


**Figure 9.** Compressive strength results of mixtures for CEM III-C including different amount of nanomaterial

3.2. Consistency, initial and final setting times

As stated before, the use of mineral additive results in higher setting times. Since high volume of slag (81%) was used in present study, this would lead to the problems of determining setting times. Therefore, only 8 mixtures of CEM I and CEM III-A were chosen and consistency, initial and final setting times were carried out for them. Consistency and setting times of experimental results are given in Figure 10-12, respectively.

As stated before, the use of mineral additive results in higher setting times. Since high volume of slag (81%) was used in present study, this would lead to the problems of determining setting times. Therefore, only 8 mixtures of CEM I and CEM III-A were chosen and consistency, initial and final setting times were carried out for them. Consistency and setting times of experimental results are given in Figure 10 and Figure 11-12, respectively.

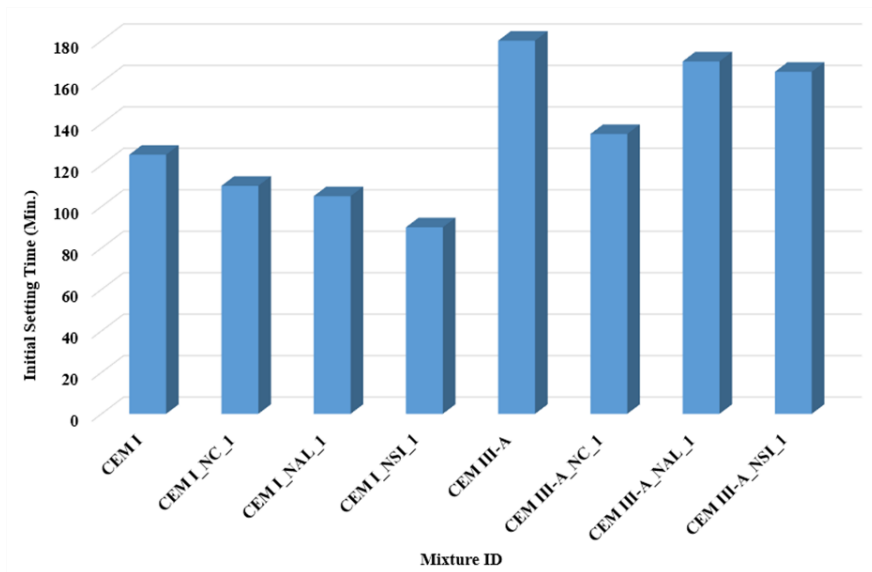


**Figure 10.** The consistency water of tailored mixtures

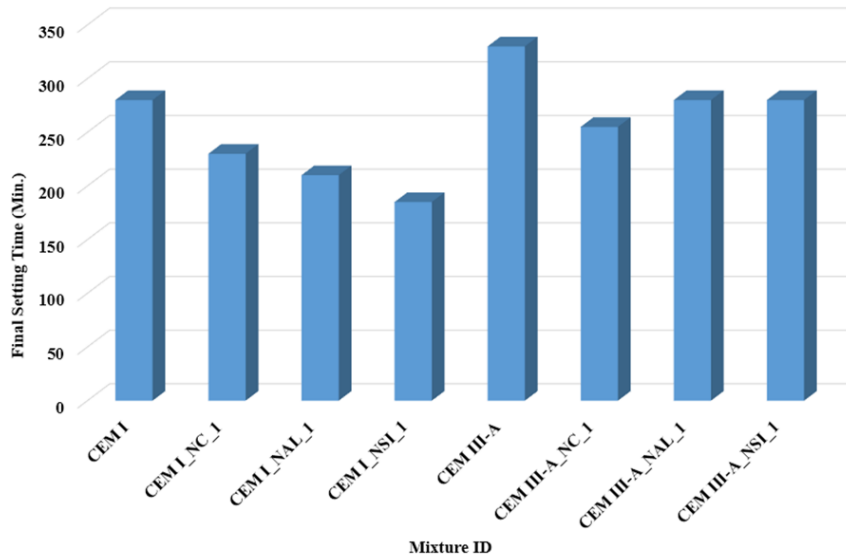
As seen in Figure 11 and Figure 12 where cement paste setting times are given, as the replacement level of slag was increased, an increase in initial and final setting times was observed (Rao and Rao, 2015). Since the setting times is depending on the hydration products, as a result of delayed pozzolanic reaction it was determined that there was an increase in both initial and final setting times. Nano sized materials promote the hydration mechanism of  $C_3S$  as nucleation effect or seeding effect, and with the effect known as chemical effect, only NC reacts with the aluminate phase of both cement and mineral admixtures which results in the formation of more hydration products, i.e., hemi- and mono-carbo aluminates. As a result of nucleation effect and chemical effect, in mixtures produced with only CEM I, there was a clear decrease in both the initial and final setting times (Sumesh et al., 2017; Gowda et al., 2017). As a result of seeding effect and reaction with calcium hydroxide formed as a result of cement hydration, the highest shortening in setting times was observed in the mixtures containing NSI while the lowest was observed in mixtures including NC.

Similar results were observed in CEM III-A type cement and CEM I in term of shortening in the setting times with the use of nanomaterial. In addition to the aforementioned discussion, since the chemical effect in addition to the nucleation effect occurred in mixtures where NC was used, the shortening setting times of the mixtures using slag with NC was higher than in CEM I with NC. Because of the increased aluminate phase in the matrix with the use of slag, NC promoted more hydration products as a result of the chemical effect, resulting in more shortening in the setting times.

As a result of the case mentioned above, it could be said that NC provided a more effective performance than that of NSI and NAL due to increasing of aluminate phase in presence of mineral admixture including cement types. Finally, it is also worth noting that the choice of nanomaterial type is very important depending on the chemical composition of mineral admixture and cementing material.



**Figure 11.** Initial setting times of selected mixtures



**Figure 12.** Final setting times of selected mixtures

#### 4. Results

In the light of all results of experimental results performed in accordance with targeted program, the following conclusions could be drawn:

- ❖ Demand in consistency water in the presence of all of the nanomaterials was increased and the lowest demand (as it had relatively small particle size) was obtained in mixtures containing NC.
- ❖ Regardless of slag replacement level, a reduction in setting times were observed in all mixtures.
- ❖ Increase in the replacement level of slag resulted in delay in setting times and also decrease in strength development of the mixtures.
- ❖ As a result of both seeding effect (NC, NAL and NS) and chemical effect (only NC) compressive strength results were enhanced regardless of curing age.
- ❖ A reduction in the increase of strength development was determined as nanomaterial replacement level was increased. The highest performance contribution was obtained in 1% usage regardless of Nano type.
- ❖ In general, in mixtures without slag, the contribution of NAL and NSI particles to the strength was higher while the effects of NC particles with slag were observed to be higher.

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#### Kaynaklar

- Abhilash, P. P., Nayak, D. K., Sangoju, B., Kumar, R. and Kumar, V. (2021). Effect of nano-silica in concrete; a review. *Construction and Building Materials*, 278, 122347. <https://doi.org/10.1016/j.conbuildmat.2021.122347>
- Aghaeipour, A. and Madhkhan, M. (2017). Effect of ground granulated blast furnace slag (GGBFS) on RCCP durability. *Construction and Building Materials*, 141, 533-541. <https://doi.org/10.1016/j.conbuildmat.2017.03.019>
- Alonso, M. C., García Calvo, J. L., Sánchez, M. and Fernandez, A. (2012). Ternary mixes with high mineral additions contents and corrosion related properties. *Materials and corrosion*, 63(12), 1078-1086. <https://doi.org/10.1002/maco.201206654>
- Atiş, C. D. and Bilim, C. (2007). Wet and dry cured compressive strength of concrete containing ground granulated blast-furnace slag. *Building and Environment*, 42(8), 3060-3065. <https://doi.org/10.1016/j.buildenv.2006.07.027>
- Bai, P., Sharratt, P., Yeo, T. Y. and Bu, J. (2014). A facile route to preparation of high purity nanoporous silica from acid-leached residue of serpentine. *Journal of nanoscience and nanotechnology*, 14(9), 6915-6922. <https://doi.org/10.1166/jnn.2014.8963>

- Bakharev, T. (2005). Durability of geopolymer materials in sodium and magnesium sulfate solutions. *Cement and Concrete Research*, 35(6), 1233-1246.  
<https://doi.org/10.1016/j.cemconres.2004.09.002>
- Barbhuiya, S., Mukherjee, S. and Nikraz, H. (2014). Effects of nano-Al<sub>2</sub>O<sub>3</sub> on early-age microstructural properties of cement paste. *Construction and Building Materials*, 52, 189-193.  
<https://doi.org/10.1016/j.conbuildmat.2013.11.010>
- Benhelal, E., Zahedi, G., Shamsaei, E., and Bahadori, A. (2013). Global strategies and potentials to curb CO<sub>2</sub> emissions in cement industry. *Journal of cleaner production*, 51, 142-161.  
<https://doi.org/10.1016/j.jclepro.2012.10.049>
- Björnström, J., Martinelli, A., Matic, A., Börjesson, L. and Panas, I. (2004). Accelerating effects of colloidal nano-silica for beneficial calcium-silicate-hydrate formation in cement. *Chemical Physics Letters*, 392(1-3), 242-248.  
<https://doi.org/10.1016/j.cplett.2004.05.071>
- Cao, M., Ming, X., He, K., Li, L. and Shen, S. (2019). Effect of macro-, micro-and nano-calcium carbonate on properties of cementitious composites—A review. *Materials*, 12(5), 781.  
<https://doi.org/10.3390/ma12050781>
- Choi, Y. C., Kim, J. and Choi, S. (2017). Mercury intrusion porosimetry characterization of micropore structures of high-strength cement pastes incorporating high volume ground granulated blast-furnace slag. *Construction and Building Materials*, 137, 96-103.  
<https://doi.org/10.1016/j.conbuildmat.2017.01.076>
- Çiftçi, M. (2020). *Nano boyutlu taneciklerin kullanımıyla yüksek hacimde yüksek fırın çürüfö içeren katkılı çimento tasarımı*. Yüksek Lisans Tezi, Batman Üniversitesi Fen Bilimleri Enstitüsü, Batman.
- Bentz, D. P., Ardani, A., Barrett, T., Jones, S. Z., Lootens, D., Peltz, M. A., ... and Weiss, W. J. (2015). Multi-scale investigation of the performance of limestone in concrete. *Construction and Building Materials*, 75, 1-10.  
<https://doi.org/10.1016/j.conbuildmat.2014.10.042>
- Demirboğa, R., Türkmen, İ. and Karakoc, M. B. (2004). Relationship between ultrasonic velocity and compressive strength for high-volume mineral-admixed concrete. *Cement and concrete research*, 34(12), 2329-2336.  
<https://doi.org/10.1016/j.cemconres.2004.04.017>
- Demirhan, S. (2017). *Nano malzemeler ile modifiye edilmiş yüksek performanslı hibrid lif donatılı betonlar*, Doktora Tezi, Gazi Üniversitesi Fen Bilimleri Enstitüsü, Ankara.
- Demirhan, S., Turk, K. and Ulugerger, K. (2019). Fresh and hardened properties of self-consolidating Portland limestone cement mortars: Effect of high-volume limestone powder replaced by cement. *Construction and Building Materials*, 196, 115-125.  
<https://doi.org/10.1016/j.conbuildmat.2018.11.111>
- Demirhan, S. (2020). Combined effects of nano-sized calcite and fly ash on hydration and microstructural properties of mortars. *Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi*, 20(6), 1051-1067.  
<https://doi.org/10.35414/akufemubid.825862>
- Duran-Herrera, A., Juárez, C. A., Valdez, P. and Bentz, D. P. (2011). Evaluation of sustainable high-volume fly ash concretes. *Cement and Concrete Composites*, 33(1), 39-45.  
<https://doi.org/10.1016/j.cemconcomp.2010.09.020>
- Elchalakani, M., Aly, T. and Abu-Aisheh, E. (2014). Sustainable concrete with high volume GGBFS to build Masdar City in the UAE. *Case Studies in Construction Materials*, 1, 10-24.  
<https://doi.org/10.1016/j.cscm.2013.11.001>
- Flower, D. J. and Sanjayan, J. G. (2007). Greenhouse gas emissions due to concrete manufacture. *The international Journal of life cycle assessment*, 12(5), 282.  
<https://doi.org/10.1065/lca2007.05.327>
- Gowda, R., Narendra, H., Rangappa, D. and Prabhakar, R. (2017). Effect of nano-alumina on workability, compressive strength and residual strength at elevated temperature of cement mortar. *Materials Today: Proceedings*, 4(11), 12152-12156.  
<https://doi.org/10.1016/j.matpr.2017.09.144>
- Hooton, R. D. (2000). Canadian use of ground granulated blast-furnace slag as a supplementary cementing material for enhanced performance of concrete. *Canadian Journal of Civil Engineering*, 27(4), 754-760.  
<https://doi.org/10.1139/100-014>
- Kong, D. L. and Sanjayan, J. G. (2008). Damage behavior of geopolymer composites exposed to elevated temperatures. *Cement and Concrete Composites*, 30(10), 986-991.  
<https://doi.org/10.1016/j.cemconcomp.2008.08.001>
- Kumar, S., Kumar, R., Bandopadhyay, A., Alex, T. C., Kumar, B. R., Das, S. K. and Mehrotra, S. P.

- (2008). Mechanical activation of granulated blast furnace slag and its effect on the properties and structure of portland slag cement. *Cement and Concrete Composites*, 30(8), 679-685. <https://doi.org/10.1016/j.cemconcomp.2008.05.005>
- Li, H., Xiao, H. G., Yuan, J. and Ou, J. (2004). Microstructure of cement mortar with nanoparticles. *Composites part B: Engineering*, 35(2), 185-189. [https://doi.org/10.1016/S1359-8368\(03\)00052-0](https://doi.org/10.1016/S1359-8368(03)00052-0)
- Li, J., Tharakan, P., Macdonald, D. and Liang, X. (2013). Technological, economic and financial prospects of carbon dioxide capture in the cement industry. *Energy Policy*, 61, 1377-1387. <https://doi.org/10.1016/j.enpol.2013.05.082>
- Li, Q. L., Chen, M. Z., Liu, F., Wu, S. P. and Sang, Y. (2015). Effect of superfine blast furnace slag powder on properties of cement-based materials. *Materials Research Innovations*, 19(sup1), S1-168. <https://doi.org/10.1179/1432891715Z.0000000001397>
- Liu, C., He, X., Deng, X., Wu, Y., Zheng, Z., Liu, J. and Hui, D. (2020). Application of nanomaterials in ultra-high-performance concrete: A review. *Nanotechnology Reviews*, 9(1), 1427-1444. <https://doi.org/10.1515/ntrev-2020-0107>
- Nazari, A. and Riahi, S. (2011). Improvement compressive strength of concrete in different curing media by Al<sub>2</sub>O<sub>3</sub> nanoparticles. *Materials Science and Engineering: A*, 528(3), 1183-1191. <https://doi.org/10.1016/j.msea.2010.09.098>
- Ng, D. S., Paul, S. C., Anggraini, V., Kong, S. Y., Qureshi, T. S., Rodriguez, C. R. and Šavija, B. (2020). Influence of SiO<sub>2</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanoparticles on the properties of fly ash blended cement mortars. *Construction and Building Materials*, 258, 119627. <https://doi.org/10.1016/j.conbuildmat.2020.119627>
- Norhasri, M. M., Hamidah, M. S. and Fadzil, A. M. (2017). Applications of using nano material in concrete: A review. *Construction and Building Materials*, 133, 91-97. <https://doi.org/10.1016/j.conbuildmat.2016.12.005>
- Orakzai, M. A. (2021). Hybrid effect of nano-alumina and nano-titanium dioxide on Mechanical properties of concrete. *Case Studies in Construction Materials*, 14, e00483. <https://doi.org/10.1016/j.cscm.2020.e00483>
- Oner, A. and Akyuz, S. (2007). An experimental study on optimum usage of GGBS for the compressive strength of concrete. *Cement and Concrete Composites*, 29(6), 505-514. <https://doi.org/10.1016/j.cemconcomp.2007.01.001>
- Özbay, E., Erdemir, M. and Durmuş, H. İ. (2016). Utilization and efficiency of ground granulated blast furnace slag on concrete properties—A review. *Construction and Building Materials*, 105, 423-434. <https://doi.org/10.1016/j.conbuildmat.2015.12.153>
- Polat, R., Demirboğa, R. and Karagöl, F. (2019). Mechanical and physical behavior of cement paste and mortar incorporating nano-CaO. *Structural Concrete*, 20(1), 361-370. <https://doi.org/10.1002/suco.201800132>
- Poudyal, L., Adhikari, K. and Won, M. (2021). Mechanical and durability properties of Portland limestone cement (PLC) incorporated with nano calcium carbonate (CaCO<sub>3</sub>). *Materials*, 14(4), 905. <https://doi.org/10.3390/ma14040905>
- Qing, Y., Zenan, Z., Deyu, K. and Rongshen, C. (2007). Influence of nano-SiO<sub>2</sub> addition on properties of hardened cement paste as compared with silica fume. *Construction and building materials*, 21(3), 539-545. <https://doi.org/10.1016/j.conbuildmat.2005.09.001>
- Rao, G. M. and Rao, T. G. (2015). Final setting time and compressive strength of fly ash and GGBS-based geopolymer paste and mortar. *Arabian Journal for Science and Engineering*, 40(11), 3067-3074. <https://doi.org/10.1007/s13369-015-1757-z>
- Rashad, A. M. (2014). A comprehensive overview about the influence of different admixtures and additives on the properties of alkali-activated fly ash. *Materials and Design*, 53, 1005-1025. <https://doi.org/10.1016/j.matdes.2013.07.074>
- Rashad, A. M. (2015). An investigation of high-volume fly ash concrete blended with slag subjected to elevated temperatures. *Journal of Cleaner Production*, 93, 47-55. <https://doi.org/10.1016/j.jclepro.2015.01.031>
- Rowles, M. and O'connor, B. (2003). Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite. *Journal of Materials Chemistry*, 13(5), 1161-1165. <https://doi.org/10.1039/B212629J>
- Şahmaran, M., Keskin, S. B., Ozerkan, G. and Yaman, I. O. (2008). Self-healing of mechanically loaded self-consolidating concretes with high volumes of fly ash. *Cement and Concrete Composites*, 30(10), 872-879. <https://doi.org/10.1016/j.cemconcomp.2008.07.001>

- Schmidt, M., Amrhein, K., Braun, T., Glotzbach, C., Kamaruddin, S. and Tänzer, R. (2013). Nanotechnological improvement of structural materials—impact on material performance and structural design. *Cement and Concrete Composites*, 36, 3-7. <https://doi.org/10.1016/j.cemconcomp.2012.11.003>
- Shaikh, F. U. A. and Hosan, A. (2019). Effect of nano silica on compressive strength and microstructures of high volume blast furnace slag and high volume blast furnace slag-fly ash blended pastes. *Sustainable Materials and Technologies*, 20, e00111. <https://doi.org/10.1016/j.susmat.2019.e00111>
- Shaikh, F. U. and Supit, S. W. (2014). Mechanical and durability properties of high volume fly ash (HVFA) concrete containing calcium carbonate (CaCO<sub>3</sub>) nanoparticles. *Construction and building materials*, 70, 309-321. <https://doi.org/10.1016/j.conbuildmat.2014.07.099>
- Sobolev, K., Flores, I., Torres-Martinez, L. M., Valdez, P. L., Zarazua, E. and Cuellar, E. L. (2009). *Engineering of SiO<sub>2</sub> nanoparticles for optimal performance in nano cement-based materials*. In Nanotechnology in construction 3 (pp. 139-148). Springer, Berlin, Heidelberg. [https://doi.org/10.1007/978-3-642-00980-8\\_18](https://doi.org/10.1007/978-3-642-00980-8_18)
- Sumesh, M., Alengaram, U. J., Jumaat, M. Z., Mo, K. H. and Alnahhal, M. F. (2017). Incorporation of nanomaterials in cement composite and geopolymer based paste and mortar—A review. *Construction and Building Materials*, 148, 62-84. <https://doi.org/10.1016/j.conbuildmat.2017.04.206>
- Sun, J., Cao, X., Xu, Z., Yu, Z., Zhang, Y., Hou, G. and Shen, X. (2020). Contribution of core/shell TiO<sub>2</sub>@ SiO<sub>2</sub> nanoparticles to the hydration of Portland cement. *Construction and Building Materials*, 233, 117127. <https://doi.org/10.1016/j.conbuildmat.2019.117127>
- Sato, T. and Diallo, F. (2010). Seeding effect of nano-CaCO<sub>3</sub> on the hydration of tricalcium silicate. *Transportation Research Record*, 2141(1), 61-67. <https://doi.org/10.3141/2141-11>
- TS EN 196-1, (2016). Çimento deney metotları-Bölüm 1: Dayanım tayini. Türk Standartları Enstitüsü.
- TS EN 196-3, (2017). Çimento deney yöntemleri-Bölüm 3: Priz süreleri ve genişleme tayini.
- TS EN 197-1, (2012). Çimento-Bölüm 1: Genel çimentolar- Bileşim, özellikler ve uygunluk kriterleri.
- Wainwright, P. J. and Rey, N. (2000). The influence of ground granulated blastfurnace slag (GGBS) additions and time delay on the bleeding of concrete. *Cement and Concrete Composites*, 22(4), 253-257. [https://doi.org/10.1016/S0958-9465\(00\)00024-X](https://doi.org/10.1016/S0958-9465(00)00024-X)
- Wang, D., Shi, C., Farzadnia, N., Shi, Z., Jia, H. and Ou, Z. (2018). A review on use of limestone powder in cement-based materials: Mechanism, hydration and microstructures. *Construction and Building Materials*, 181, 659-672. <https://doi.org/10.1016/j.conbuildmat.2018.06.075>
- Wu, Q., Miao, W. S., Zhang, Y. D., Gao, H. J. and Hui, D. (2020). Mechanical properties of nanomaterials: A review. *Nanotechnology Reviews*, 9(1), 259-273. <https://doi.org/10.1515/ntrev-2020-0021>
- Yalçınkaya, Ç. and Yazıcı, H. (2017). Effects of ambient temperature and relative humidity on early-age shrinkage of UHPC with high-volume mineral admixtures. *Construction and Building Materials*, 144, 252-259. <https://doi.org/10.1016/j.conbuildmat.2017.03.198>
- Yang, H., Che, Y. and Leng, F. (2018). High volume fly ash mortar containing nano-calcium carbonate as a sustainable cementitious material: microstructure and strength development. *Scientific reports*, 8(1), 1-11. <https://doi.org/10.1038/s41598-018-34851-4>
- Zaitri, R., Bederina, M., Bouziani, T., Makhoulfi, Z. and Hadjoudja, M. (2014). Development of high performances concrete based on the addition of grinded dune sand and limestone rock using the mixture design modelling approach. *Construction and Building Materials*, 60, 8-16. <https://doi.org/10.1016/j.conbuildmat.2014.02.062>
- Zhao, Y., Qiu, J., Xing, J. and Sun, X. (2020-a). Chemical activation of binary slag cement with low carbon footprint. *Journal of Cleaner Production*, 267, 121455. <https://doi.org/10.1016/j.jclepro.2020.121455>
- Zhao, Z., Qi, T., Zhou, W., Hui, D., Xiao, C., Qi, J. and Zhao, Z. (2020-b). A review on the properties, reinforcing effects, and commercialization of nanomaterials for cement-based materials. *Nanotechnology Reviews*, 9(1), 303-322. <https://doi.org/10.1515/ntrev-2020-0023>
- Zhuang, S. and Wang, Q. (2021). Inhibition mechanisms of steel slag on the early-age hydration of cement. *Cement and Concrete Research*, 140, 106283. <https://doi.org/10.1016/j.cemconres.2020.106283>