

INNOVATIVE NANOPARTICLE-BASED ADMIXTURE FOR SUSTAINABLE CONSTRUCTION MATERIALS AND TECHNOLOGIES

Van Bui*), Chris Eagon, Steve Schaefer and Paul Seiler
BASF Corporation, 23700 Chagrin Blvd., Beachwood, Ohio 44122, USA

**) Contact author's email: van.bui@basf.com*

ABSTRACT

Concrete plays a vital part in our daily lives. However, the production of concrete, notably cement, pose sustainability issues that need to be managed. To improve the sustainability of concrete, an innovative admixture, which contains Calcium Silicate Hydrate (C-S-H) particles, was recently developed at BASF Corporation. The patent-pending admixture can significantly enhance concrete strength at both early and late ages. Compared with mortar mixes without the admixture, the mortar mixes containing the newly developed admixture and 65% slag, 30% fly ash or 35% milled limestone exhibited 1-day strength increase of 65%, 59% or 45%, respectively. Similarly, compared with mortar mixes without the admixture the mortar mixes containing the newly developed admixture and 65% slag, 30% fly ash or 35% milled limestone exhibited 28-day strength increase of 28%, 32% or 24%, respectively. The use of this concrete admixture also enables a higher replacement of portland cement with supplementary materials such as fly ash, slag cement and milled limestone. In other hand, this innovative admixture can also enhance a reduction of considerable amount of cementitious materials, typically in range from 30 kg/m³ to 60 kg/m³. Thanks to the reduction of portland cement consumption in concrete, the use of this new admixture can contribute to reduce CO₂-footprint. The information presented will show the use of nanoparticle-based liquid admixtures provides options to modify and improve fresh properties and strength of concrete.

Keywords: Admixture, Calcium-Silicate-Hydrate, Concrete, Nanoparticle, Strength, Strength-Enhancement, Supplementary Materials, Sustainability

INTRODUCTION

Nowadays sustainability in construction materials and technologies is of special attention in many countries around the world. Many R&D efforts have been focusing on how to reduce CO₂-footprint, material usage and energy consumption in construction industry. Concrete plays a vital part in our daily lives, however, the

production of concrete, notably cement, pose sustainability issues that need to be managed (Hanle et al.; Rubenstein, 2012). To improve the sustainability of concrete, scientists are turning toward nanotechnology solutions (Bjornstrom et al., 2009, Collepardi et al., 2002, Li, 2004, Porro et al., 2005, Scrivener, 2009 and Sobolev et al, 2012). One of the nanotechnology solutions is development of an admixture containing Calcium Silicate Hydrate (C-S-H) particles which improve the cement hydration process and provide a way to reduce the cementitious material content. This brings a significant contribution to the sustainability in construction by limiting the use of natural resources, conserving energy and reducing CO₂-emissions. An innovative C-S-H nanoparticle-containing admixture (the Master X-Seed 55 admixture, hereafter called NPA) was recently developed at BASF Corporation (see reference in BASF document). The patent-pending admixture can significantly enhance concrete strength at both early and late ages. The use of this concrete admixture enables a higher replacement of portland cement with supplementary materials such as fly ash, slag cement and milled limestone. In other hand, this innovative admixture can also enhance a reduction of considerable amount of cementitious materials. Thanks to the reduction of portland cement consumption in concrete, the use of this new admixture also contributes to reduce CO₂-footprint. The use of the admixture can also contribute to reduce energy needed in concrete curing and enhance earlier transportation of cast elements as well as increase of construction speed.

The information presented will show the use of nanoparticle-based liquid admixtures provides options to modify and improve the fresh properties and strength of concrete. This paper will present test results evaluated with mortar and concrete mixtures.

TEST RESULTS AND DISCUSSIONS

NPA's Strength-Enhancement for Mixes with High Supplementary Materials Contents

Mortars containing Portland cement and different contents of Class F fly ash (30%, 40% and 50% replacement), slag cement (65% replacement) or milled limestone (35% replacement) were evaluated. The evaluation program has been presented in detail in other publication (Seiler et al, 2017). Mortars had water-to-cementitious materials ratio (w/cm) of 0.51 and 0.40. Batch compositions of mortars and test results are shown in Table 1 and 2. The strength test results can be also seen in Fig. 1 and 2.

Table 1: Fly Ash Containing Mortars and Test Results

Mix ID	FA30, No-NPA	FA30, NPA	FA40, No-NPA	FA40, NPA	FA50, No-NPA	FA50, NPA
Cement (g)	1029	1029	882	882	770	770
Fly ash (g)	411	411	588	588	770	770
Sand (g)	2500	2500	2500	2500	2500	2500
w/cm	0.51	0.51	0.51	0.51	0.40	0.40

NPA (mL/100 kg)		1150		1150		820
Flow (mm)	188	204	190	206	112	110
Compressive strength (MPa)						
1 day	6.76	10.76	5.79	8.97	7.59	10.41
7 days	21.17	32.28	18.76	25.66	17.38	23.24
28 days	34.97	46.07	31.10	38.48	27.72	37.03

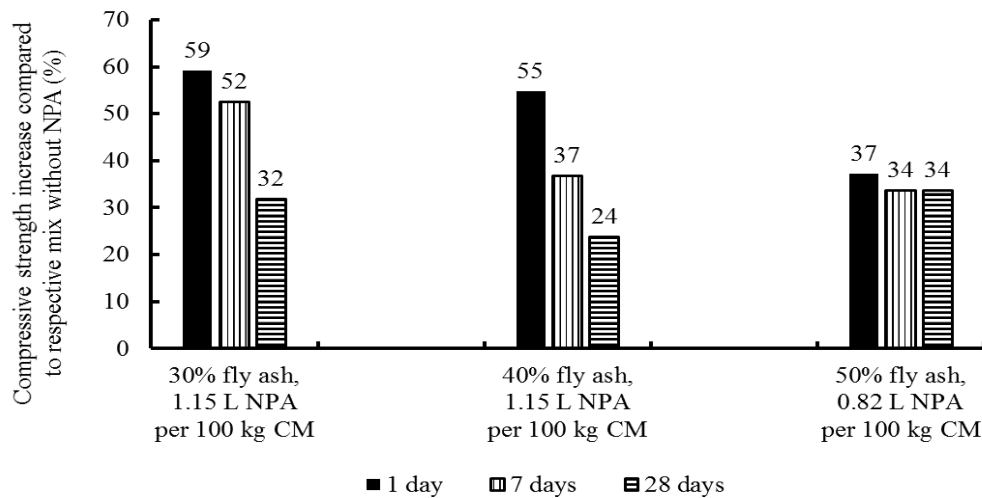


Fig. 1: Compressive strength increase of fly ash containing mortars with NPA admixture in comparison with respective no-NPA mortars

As can be seen in Table 1 and Fig. 1, for the same w/cm of 0.51 and 30% fly ash replacement, mortar with NPA exhibited strength at age of 1 day, 7 days and 28 days, being 59%, 52% and 32%, respectively, higher than that of respective mortar without NPA. Similarly, for the same w/cm of 0.51 and 40% fly ash replacement, mortar with NPA exhibited strength at age of 1 day, 7 days and 28 days, being 55%, 37% and 24%, respectively, higher than that of respective mortar without NPA. For the same w/cm and the same dosage of NPA, NPA-mix with lower fly ash replacement (30%) had higher respective percentage increase of strength at all ages than NPA-mix with higher fly ash replacement (40%). This suggests that NPA influences more on the hydration process of Portland cement.

Fig. 1 also shows that, for the same w/cm of 0.40 and 50% fly ash replacement, mortar with NPA exhibited strength at age of 1 day, 7 days and 28 days, being 37%, 34% and 34%, respectively, higher than that of respective mortar without NPA.

Table 2: Slag Cement/Milled Limestone Containing Mortars and Test Results

Mix ID	SL65, ref.	SL65, NPA	LS35, ref.	LS35, NPA
Cement (g)	539	539	1001	1001
Ground slag (g)	1001	1001		

Milled limestone (g)			539	539
Sand (g)	2500	2500	2500	2500
w/cm	0.45	0.45	0.40	0.40
NPA (mL/100 kg)		1920		1920
Flow (mm)	107	142	105	115
Compressive strength (MPa) at age:				
1 day	6.62	10.90	15.52	22.55
7 days	33.33	53.63	31.29	40.88
28 days	55.10	70.48	40.34	50.00

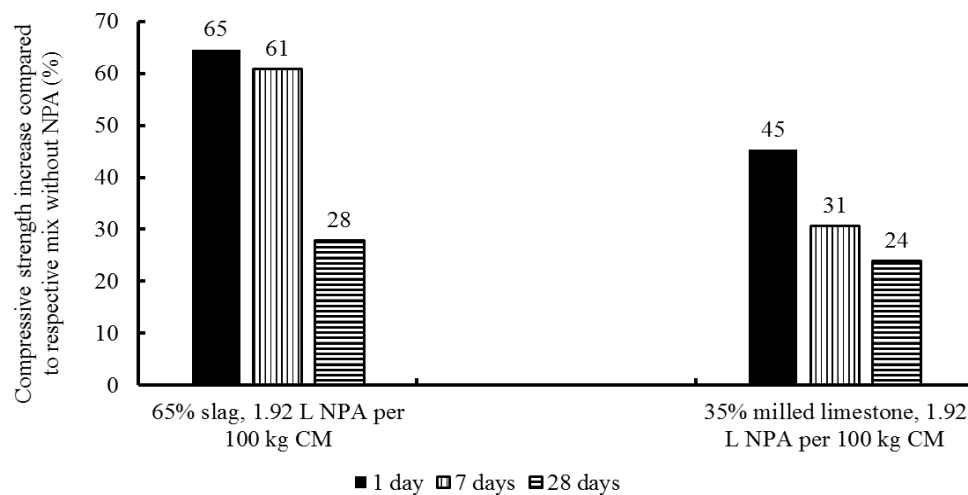


Fig. 2: Compressive strength increase of slag/milled limestone containing mortars with NPA admixture in comparison with respective no-NPA mortars

As can be seen from Table 2 and Fig. 2, for the same w/cm of 0.45 and 65% slag replacement, mortar with NPA exhibited strength at age of 1 day, 7 days and 28 days, being 65%, 61% and 28%, respectively, higher than that of respective mortar without NPA. Similarly, for the same w/cm of 0.40 and 35% milled-limestone replacement, mortar with NPA exhibited strength at age of 1 day, 7 days and 28 days, being 45%, 31% and 24%, respectively, higher than that of respective mortar without NPA.

NPA's Strength Enhancement for Wide Ranges of Concrete Mixtures

Examples of using NPA in non-air-entrained concrete mixtures with different ratios (w/cm) between water and total cementitious materials and different supplementary materials (SM) can be seen in Tables 3, and from Fig. 3 to Fig. 5. Compressive strengths of non-air-entrained concrete mixtures with different water to cement ratios (w/c) and Portland cement only are illustrated in Fig. 6 and 7. Fig. 8 shows the strength development of air-entrained concrete mixtures without and with NPA.

Table 3: Proportions and Test Results of Concrete with Different w/cm Ratios

Mix ID	0.53w/c m, No- NPA	0.53w/c m, NPA	0.45w/c m, No- NPA	0.45w/c m, NPA	0.29w/c m, No- NPA	0.29w/c m, NPA
Concrete materials (kg/m ³)						
Cement	268	268	290	290	237	237
Fly ash	67	67	73	73		
Ground Slag					356	356
Silica fume					12	12
Coarse aggregate	1122	1122	1122	1122	949	949
Sand	740	740	752	752	653	653
Water	177	177	163	163	176	176
w/cm	0.530	0.530	0.450	0.450	0.290	0.290
Design air (%)	2.5	2.5	2.5	2.5	2.0	2.0
Chemical admixtures (mL/100 kg cementitious materials)						
Superplasticizer	0	0	196	163	635	596
NPA	0	980	0	980	0	490

Table 3: Proportions and Test Results of Concrete with Different w/cm Ratios (cont'd)

Mix ID	0.53w/c m, No- NPA	0.53w/c m, NPA	0.45w/c m, No- NPA	0.45w/c m, NPA	0.29w/c m, No- NPA	0.29w/c m, NPA
Slump (mm)	171	165	171	178		
Slump flow (mm)					616	641
Air (%)	2.9	2.6	2.7	3.1	2.0	2.1
Compressive strength (MPa) at:						
1 day	12.28	15.24	19.31	21.79	25.86	28.14
7 days	24.28	30.14	31.59	38.97	74.48	72.07
28 days	33.59	40.34	41.52	50.69	93.17	99.79
56 days	No-test	No-test	No-test	No-test	96.55	103.66

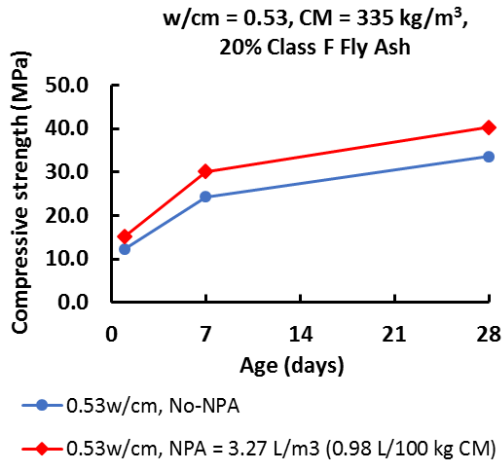


Fig. 3: Concrete with w/cm of 0.53 and 20% fly ash

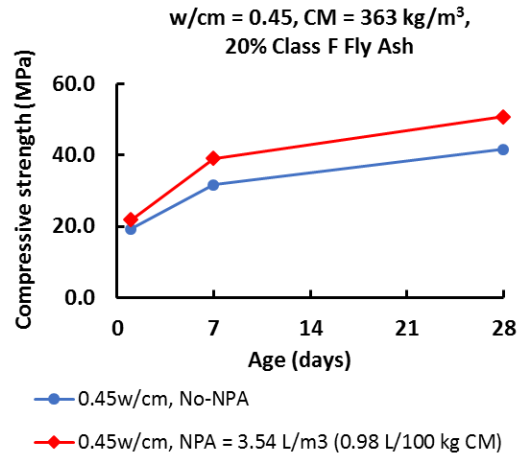


Fig. 4: Concrete with w/cm of 0.45 and 20% fly ash

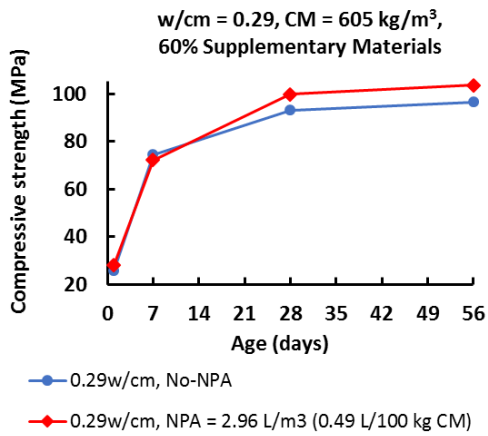


Fig. 5: Concrete with w/cm of 0.29 and 60% supplementary materials

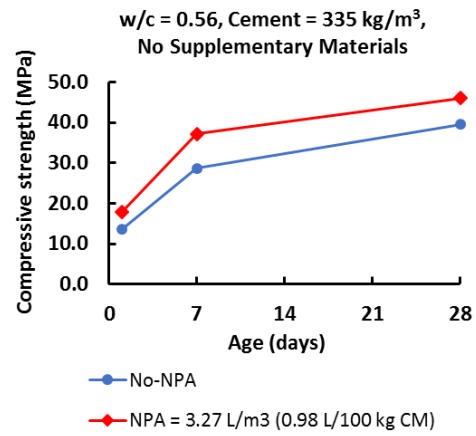


Fig. 6: Concrete with w/c of 0.56 and Portland cement only

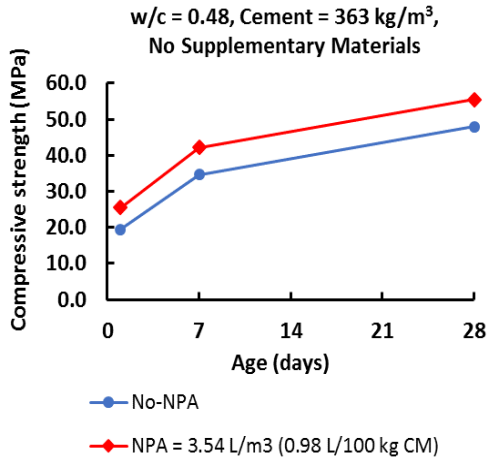


Fig. 7: Concrete with w/c of 0.48 and Portland cement only

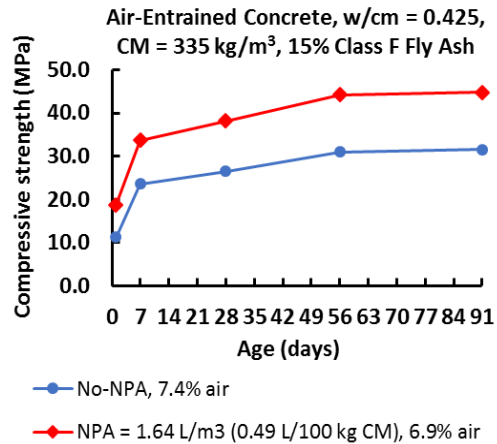


Fig. 8: Air-entrained concrete without and with NPA

As can be seen in Table 3 and from Fig. 3 to Fig. 7, NPA increases considerably strength at early and late ages for the wide ranges of non-air-entrained concrete mixtures with different w/cm (i.e. 0.56, 0.53, 0.48, 0.45 and 0.29) and different contents of supplementary materials (i.e. 0%, 20% and 60%). Fig. 8 shows significant strength enhancement of NPA for air-entrained concrete mixture. The conclusion is that NPA can be used to increase strength of concrete mixtures for a wide construction application.

Use of NPA for Reduction of Cementitious Materials in Concrete Mixtures

The compositions and test results of concrete mixtures with reduced cementitious materials are shown in Table 4, 5 and 6, and from Fig. 9 to Fig. 11, inclusively.

As can be seen in Table 4 and Fig. 9, for use of Portland cement only, mixtures with NPA and cement reduction of 30 kg/m³, 45 kg/m³ and 60 kg/m³ and higher w/c (0.58, 0.59 and 0.60) exhibited similar or greater strength at ages of 1 day, 7 days and 28 days in comparison with non-NPA mixture with higher cement content and lower w/c (0.56).

Similarly, for use of 15% ground slag, mixtures with NPA and cementitious material reduction of 30 kg/m³, 45 kg/m³ and 60 kg/m³ and higher w/cm (0.364, 0.372 and 0.382) exhibited similar or greater strength at ages from 1 day, 7 days, 28 days, 56 days and 90 days in comparison with non-NPA mixtures with higher cementitious material content and lower w/cm (0.351) (see Table 5 and Fig. 10).

For the use of 15% fly ash, mixtures with NPA and cementitious material reduction of 48 kg/m³ and 52 kg/m³ and higher w/cm (0.595 and 0.61) exhibited similar or greater strength at ages of 1 day, 7 days and 28 days in comparison with non-NPA mixtures with higher cementitious material content and lower w/cm (0.56) (see Table 6 and Fig. 11). The cementitious material reduction, thanks to use of NPA, contributes to reduce CO₂-foot print, as production of cement generates high CO₂-emissions into environment.

Table 4: Composition and Test Results of Mixtures with NPA and Cement Reduction

Mix ID	O-CR, ref.	30-CR, NPA	45-CR, NPA	60-CR, NPA
Concrete materials (kg/m ³)				
Cement	335	305	290	275
CM reduction*	0	30	45	60
Coarse aggregate	1122	1135	1135	1135
Sand	734	772	799	826
w/cm	0.56	0.58	0.59	0.60
Design air (%)	2.5	2.5	2.5	2.5
NPA (L/m ³)	0	0.96	1.37	1.73
Slump (mm)	191	178	178	171
Measured air (%)	1.9	2.0	2.0	2.0
Compressive strength (MPa)				
1 day	12.48	14.83	14.48	14.41
7 days	27.10	30.41	32.07	32.07
28 days	37.17	43.38	42.14	45.17

*Note: * Cement reduction compared with reference mix (Mix O-CR, ref.)*

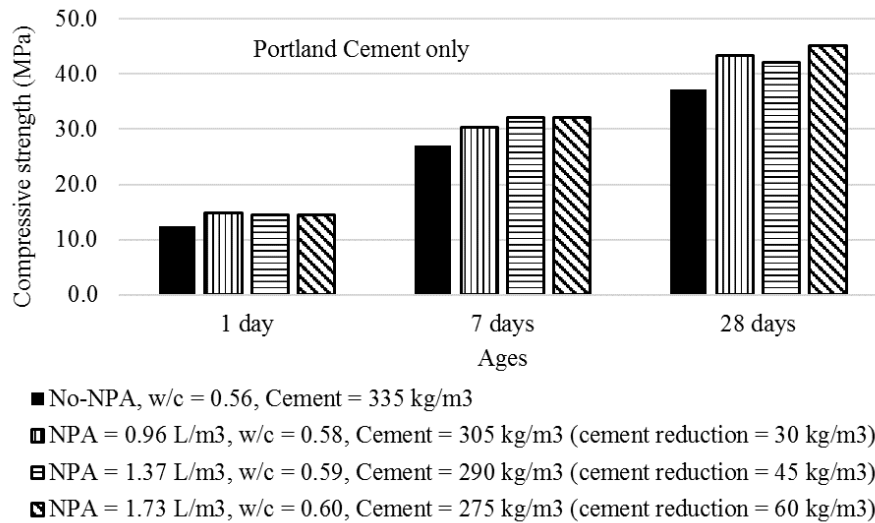


Fig. 9: Compressive strength of NPA-containing concrete with different amounts of Portland cement reduction compared with that of concrete without NPA

Table 5: Composition and Test Results of NPA-Mixtures and CM Reduction

Mix ID	O-CR, ref.	30-CR, NPA	45-CR, NPA	60-CR, NPA
Concrete materials (kg/m ³)				
Cement	393	367	354	342
Ground slag	69	65	63	60
CM reduction*	0	30	45	60
Coarse aggregate	1127	1139	1154	1154
Sand	718	709	724	742

w/cm	0.351	0.364	0.373	0.382
Table 5: Composition and Test Results of NPA-Mixtures with CM Reduction (cont'd)				
Mix ID	O-CR, ref.	30-CR, NPA	45-CR, NPA	60-CR, NPA
Design air (%)	2.5	2.5	2.5	2.5
NPA (L/m ³)	0	1.37	1.97	2.53
Superplasticizer (mL/100 kg CM)	254	287	280	287
WRA** (mL/100 kg CM)	261	196	196	209
Slump (mm)	210	203	210	210
Measured air (%)	2.9	2.7	2.4	2.4
Compressive strength (MPa)				
1 day	21.66	23.59	26.76	21.52
7 days	51.93	55.93	55.45	56.34
28 days	68.07	69.38	68.83	66.07
56 days	70.55	72.00	71.59	73.59
90 days	71.66	75.24	76.76	78.83
Note: * Cementitious materials (CM) reduction compared with reference mix (Mix O-CR, ref.)				
** WRA is water-reducing admixture				

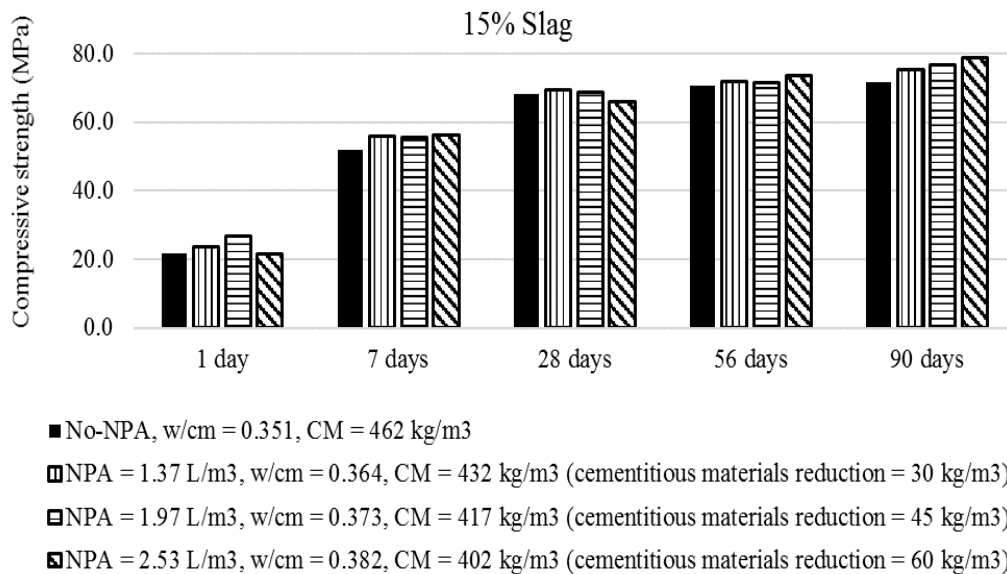


Fig. 10: Compressive strength of NPA-containing concrete with different amounts of cementitious material reduction compared with that of concrete without NPA

Table 6: Composition and Test Results of NPA-Mixtures and CM Reduction

Mix ID	O-CR, ref.	48-CR, NPA	52-CR, NPA
Cement (kg/m ³)	261	220	217

Fly ash (kg/m ³)	46	39	38
CM reduction* (kg/m ³)	0	48	52

Table 6: Composition and Test Results of NPA-Mixtures and CM Reduction (cont'd)

Mix ID	O-CR, ref.	48-CR, NPA	52-CR, NPA
Coarse aggregate (kg/m ³)	1122	1135	1135
Sand (kg/m ³)	785	860	857
w/cm	0.560	0.595	0.610
Design air (%)	2.5	2.5	2.5
NPA (L/m ³)	0	1.42	1.99
Slump (mm)	216	146	184
Measured air (%)	2.3	2.3	2.2
Compressive strength (MPa)			
1 day	10.97	12.21	13.59
7 days	23.45	27.10	24.07
28 days	31.72	36.00	34.55

*Note: * Cementitious materials (CM) reduction compared with reference mix (Mix O-CR, ref.)*

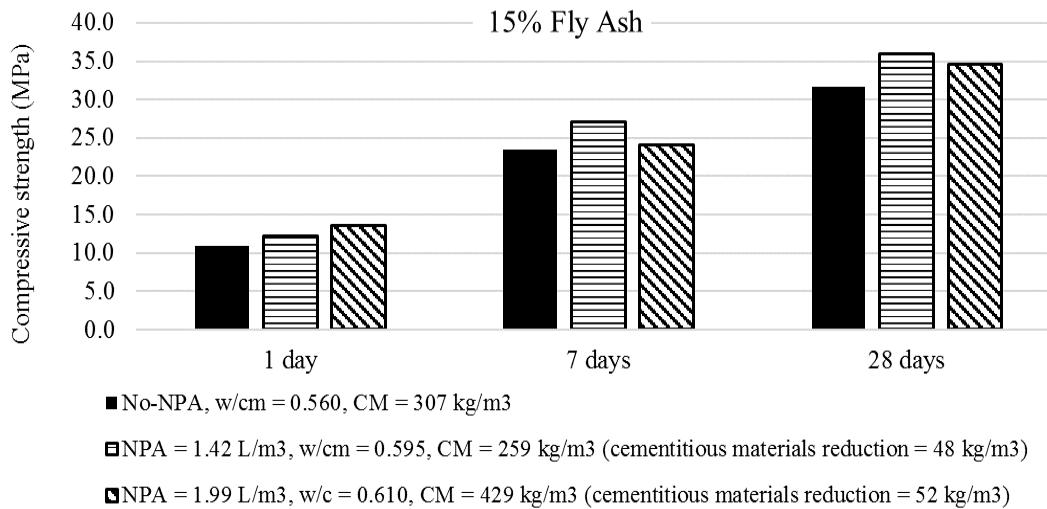


Fig. 11: Compressive strength of NPA-containing concrete with different amounts of cementitious material reduction compared with that of concrete without NPA

NPA Enhancement of Early-Age Strength of Concrete Mixtures

NPA was used in evaluating its enhancement of early-age strength of concrete mixtures, which are typically used in precast/prestressed concrete application. Cement content of 445 kg/m³ and 337 kg/m³ and w/c of 0.371 and 0.398, respectively were used in concrete mixtures without and with NPA (see Table 7). Test results in Table 7 and Fig. 12 show that, for the same w/c and the same cement content, concrete with NPA exhibited significantly higher 16-h strengths than those of concrete without NPA. This implies that use of NPA can reduce a time of curing or heat curing for precast/prestressed concrete elements. The test results also show that NPA-concrete with lower cement content (337 kg/m³) had higher 16-h strength (29.2 MPa) than that

(26.9 MPa) of non-NPA concrete with higher cement content (445 kg/m³). One can conclude that the use of NPA enhances the sustainability thanks to the reduction of cement consumption and energy needed for heat-curing in manufacturing precast/prestressed concrete elements.

Table 7: Composition and Early-Age Strength of NPA-Containing Concrete

Mix ID	445C, No-NPA	445C, NPA	337C, No-NPA	337C, NPA
Cement (kg/m ³)	445	445	377	377
Coarse aggregate (kg/m ³)	1071	1071	1129	1129
Natural Sand (kg/m ³)	682	682	719	719
Water (kg/m ³)	165	165	150	150
w/c	0.371	0.371	0.398	0.398
Design air (%)	2.0	2.0	2.0	2.0
Superplasticizer (mL/100 kg CM)	522	522	522	522
NPA (mL/100 kg CM)	0	652	0	652
Slump (mm)	203	203	203	203
Measured air (%)	1.5	2.0	1.6	2.1
16-h compressive strength (MPa)	26.9	35.7	23.4	29.2

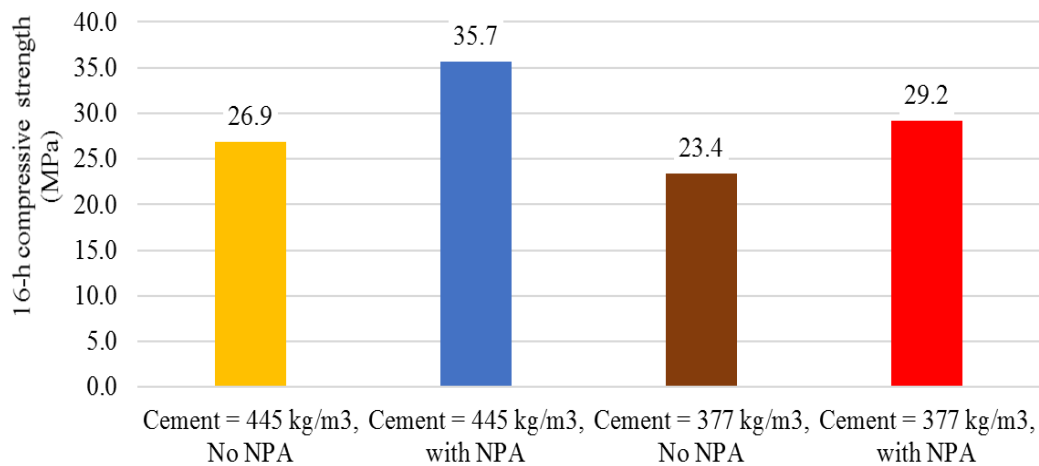


Fig. 12: Early-age compressive strength of NPA-containing concrete with different cement contents

SUMMARY

The newly-developed nanoparticle-containing admixture (NPA) significantly increases concrete strength at both early and late ages. It can enhance a replacement of high Portland cement content with supplementary materials in concrete mixtures. The use of the nanoparticle-containing admixture can also reduce considerably the cementitious

material consumption and/or energy needed for heat-curing of concrete elements. Thanks to high early-age strength of NPA concrete, the cast elements can be shipped earlier to construction site and lead to increase of construction speed. Thus, use of the innovative nanoparticle-containing admixture can contribute to reduce CO₂-foot print and enhance sustainability in concrete production and construction technologies.

REFERENCES

- BASF document “Master X-Seed 55 – Strength Enhancing Admixture”
<https://www.master-builders-solutions.basf.us/en-us/products/concrete-admixtures/increasing-concrete-strength/master-x-seed-55>.
- Bjornstrom, J., Martinelli, A., Matic, A., Borjesson, L., Panas, I. (2004) “Accelerating Effects of Colloidal Nano-Silica for Beneficial Calcium-Silicate-Hydrate Formation in Cement”, *Chem Phys Lett*, 2004;392(1-3): pp. 242-248.
- Colleparidi, M., Ogoumah-Olagot, J.J., Skarp, U., Troli, R., (2002) “Influence of Amorphous Colloidal Silica on the Properties of Self-Compacting Concretes”, *Proceedings of the International Conference on Challenges in Concrete Construction - Innovations and Developments in Concrete Materials and Construction*, Dundee, UK, 2002, pp. 473 - 483.
- Hanle, L. J., Jayaraman, K. R., and Smith J. S. “CO₂ Emissions Profile of the U.S. Cement Industry”, <https://www3.epa.gov/ttnchie1/conference/ei13/ghg/hanle.pdf>
- Li, G. (2004) “Properties of High-Volume Fly Ash Concrete Incorporating Nano-SiO₂”, *Cement and Concrete Research Journal*, 34, 2004, pp.1043-1049.
- Porro, A., Dolado, J.S., Campillo, I., Erkizia, E., de Miguel, Y., Sáez de Ibarra, Y., and Ayuela, A. (2005) “Effects of nanosilica additions on cement pastes; *Applications of Nanotechnology in Concrete Design*, Thomas Telford; London.
- Rubenstein, M. (2012) “Emissions from the Cement Industry”, Earth Institute, Columbia University, May 9, 2012,
<https://blogs.ei.columbia.edu/2012/05/09/emissions-from-the-cement-industry>.
- Scrivener, K.L. (2009) “Nanotechnology and Cementitious Materials” in Z. Bittnar, P.J.M. Bartos, J. Nemecek, V. Smilauer, and J. Zeman, Editors. *Nanotechnology in construction: Proceedings of the NICOM3 (3rd International Symposium on Nanotechnology in Construction)*: Prague, Czech Republic, 2009. p. 37-42.
- Seiler, P. H., Eagon, C., Ong, F. S., Farrington, S. A. and Bui, V. (2017) “A New Generation of Micro-Particulate-Based Admixtures for Concrete”, *ACI Special Publication*, Volume 320, pp. 22.1-22.16.

Sobolev, K., Sanchez F., and Flores I. (2012) “The Use of Nanoparticle Admixtures to Improve the Performance of Concrete”, *Proceedings of 12th International Conference on Recent Advances in Concrete Technology and Sustainability Issues*, pp. 455-469.