- Technical Paper -

STRENGTH DEVELOPMENT IN SLAG CONCRETE USING C-S-H AND NITRATE/NITRITE ACCELERATORS AT VARIOUS CURING CONDITIONS

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ABSTRACT

This study evaluates the performance of two hardening accelerators – C-S-H seeding-based ACX and nitrate/nitrite-based ACN – in slag concrete mixes with Ordinary (N) or High early strength (H) Portland cements under steam and standard curing conditions. Use of ACX or ACN enabled H slag concretes to achieve early age strengths comparable to N mixes under lower curing temperatures, allowing faster demolding times without affecting long-term strength. ACX consistently enhanced early-age strength across all conditions, while ACN showed delayed effectiveness at low temperature.

Keywords*:* C-S-H based accelerator, blast-furnace slag, compressive strength, curing temperature

1 INTRODUCTION

Japan has announced in October 2020, its target of reducing CO_2 emissions to net zero by 2050. Cement and concrete industries have come together to commit to producing carbon neutral concrete by 2050. Use of supplementary cementitious materials (SCMs) such as granulated blast furnace slag (GBFS), or simply slag, as partial replacement for cement has consistently been one of the most effective strategies for reducing the carbon footprint of the construction industry. However, concrete mixed with slag exhibit delayed setting times and slower strength development, making it unsuitable for applications that require high initial strength, such as precast concrete. Precast concrete industry contributes to CO_2 emissions during curing processes as well, especially during the heating and high constant temperature stages that are mandatory to achieve rapid development in early strength.

Hardening accelerators are typically used in concrete to shorten set times or to increase early strength development or both. Accelerators can be broadly classified into – soluble inorganic salts; soluble organic salts; and insoluble seeding material. Calcium chloride is the most used inorganic salt for strength development but is understandably avoided due to its susceptibility to corrosion of steel reinforcement. Strengthening effect of most organic salts like alkanolamines is generally low and hence, are rather used as grinding aids due to their efficiency in improving rheological properties [1].

Among chloride or alkali-free accelerators, use of nitrate/nitrite-based accelerators has been prevalent in admixture industry over the past decade. However, using large amounts of such accelerators lead to issues such as increase in cracking, decrease in resistance to chloride ion penetration under severe environments [2].

One of the latest approaches to using accelerators involves nucleation seeding with water-based suspensions of stabilized C-S-H nanoparticles, shortly referred to as C-S-H seeding. This method has been favourably reviewed [3, 4] as it does not show any adverse effects on long-term mechanical strength or durability. Studies [5, 6] have also demonstrated the effectiveness of alkali-free C-S-H seeding-based hardening accelerator as strength enhancer for slag concrete, even in mixes where 70% of cement was replaced with slag under various curing conditions.

Although using high proportions of slag in concrete reduces CO_2 emissions, the benefit is offset through energy consumed during curing conditions at elevated temperatures, that are employed for obtaining desired strength development. A growing trend in precast industry to optimally lower CO_2 emissions by enabling higher proportion of binder replacement with slag and achieving desired performance through minimal environmental load during curing is by using blends of High early strength Portland cement and slag. Studies have shown that blending 50% High early strength Portland cement with 50% blast furnace slag, having specific surface area over 6000 m^2/g, can produce concrete with desirable initial strength development, excellent durability, and minimal cost implications without using additional admixtures [7]. However, obtaining slag with such high specific surface area is challenging. This study explores the possibility of achieving related results using blends of High early strength Portland cement and commercially available slags (specific surface area ~ 4000 m^2/g). The impact of using two types of hardening accelerators – ACX, a C-S-H seeding-based hardening accelerator; and ACN, a nitrite/nitrate-based hardening accelerator is evaluated in blends of high early strength Portland cement and slag at set temperatures under various curing methods.

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2 EXPERIMENTAL PROCEDURE

2.1 Raw materials and Apparatus

Tables 1 and 2 describes the raw materials used for experiments with their physical characteristics and concrete characteristics measured in this study along with the test method standards.

Table 3 describes the concrete mix designs used throughout this study. The water-to-binder ratio (W/B) is set to 40%. The binder used in the mix design is prepared by mixing N or H cements with GBFS in three ratios – 100:0, 60:40 and 30:70. Fresh concrete is mixed using a twin-shaft mixer of 55L capacity. The target fresh properties of concrete are slump within 18 ± 2.5 cm. and air content below 2.0%. The dosage of the superplasticizer (SP) is adjusted to meet the prescribed slump and air content. The performance in terms of setting time, compressive strength with and without hardening accelerators – ACX and ACN, is evaluated. To do so, each concrete mix with three levels of dosages of AC – 0.0%, ACX – 4.0% and ACN – 4.0% by weight of binder, were mixed. Slump and air were measured for each batch while casting specimens to measure setting time, compressive strength.

2.2 Outline of this study

The outline of this study is to

1. Compare the performance of ACX and ACN in slag concrete with N cement under steam and standard curing at room temperature (20°C).
2. Evaluate the performance of ACX and ACN in slag concrete with H cement at similar slag replacement ratios as (1) under steam curing (at lower temperature) and standard curing at 20°C.
3. Assess strength development in slag concrete with H cement at higher and lower ambient curing temperature i.e., 5°C and 35°C.
4. Perform calorimeter analyses of slag-N cement pastes at 5°C and 20°C, to identify the cause for difference in strength enhancement behavior of ACX and ACN at these temperatures.

2.3 Curing method(s)

Figs. 1 and 2 (and Table 3) describe the curing conditions used for each mix throughout this study.

In precast concrete with N cement, the most used curing method involves 3 hours of steam curing at 60°C. However, the hydration rate of GBFS is more sensitive to temperature than that of Portland cement and thus, slag concretes with particularly high slag content (~ 70%) can exhibit higher strength at such elevated curing temperatures [5]. To assess strength enhancement with and without accelerator, the curing temperature for N30 was set at 40°C, while N60 and N100 were cured at 60°C.

The curing temperature for H100, H60, and H30 mixes was set at 40°C to evaluate whether their strength development is comparable to slag concrete mixes made with N-type cement.

As the hydration of slag is sensitive to temperature, it is also crucial to study the influence of pre-curing and post-curing temperature on strength development.

Table 1 Physical properties of Raw materials

RM	Symbol	Physical properties
Water	W	Tap water
Cement	N	Ordinary Portland Cement Density = 3.16 g/cm^3, Specific surface area = 3,240 cm^2/g
	H	High early strength Portland Cement Density = 3.14 g/cm^3, Specific surface area = 4,570 cm^2/g
Slag	GBFS	Granulated blast furnace slag Density = 2.89 g/cm^3, Specific surface area = 4,350 cm^2/g
Sand	S	Sand from Oi River system Surface dry density = 2.59 g/cm^3, Surface moisture content = 1.94%
Gravel	G	Crushed hard stone from Ome Surface dry density = 2.65 g/cm^3, Maximum dimension = 20 mm
Admixtures	SP	High range water reducer Polycarboxylate ether-based component
	ACX	C-S-H based hardening accelerator
	ACN	Nitrate/Nitrite based hardening accelerator

Table 2 Evaluation items

Characteristic	Test Method
Slump	JIS A 1101
Air content	JIS A 1128
Concrete Temperature (C.T)	JIS A 1156
Setting time	JIS A 1147
Compressive strength	JIS A 1106 Specimen dimensions: φ10 × 20 cm. Measured at: (Steam cured) 7h, 18h, 14d (Standard curing) 24h, 3d, 7d, 28d

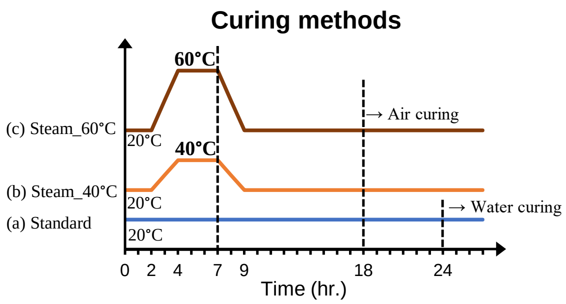

Fig.1 Curing methods used in (1), (2)

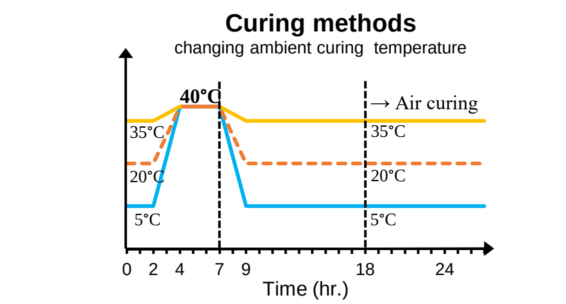

Fig. 2 Curing methods used in (3)

To do so, strength development in slag concretes mixed with H cement is evaluated when the curing temperature before and after heating to 40°C is kept at 5°C and 35°C, as shown in Fig. 2.

Table 3 Concrete Mix designs used in this study

Mix	W/B (%)	s/a (%)	Unit RM weight (kg/m^3)						Curing method (*Fig.* 1)	
			W	N	H	GBFS	S	G	Steam	Standard
N100	40.0	42.7	165	413	-	-	759	1048	(c)	(a)
N60		42.2	165	248	-	165	746	1048	(c)	(a)
N30		41.9	165	124	-	289	736	1048	(b)	(a)
H100		42.6	165	-	413	-	757	1048	(b)	(a)
H60		42.2	165	-	248	165	745	1048	(b)	(a)
H30		41.9	165	-	124	289	736	1048	(b)	(a)

2.4 Isothermal calorimeter analysis

Isothermal calorimetry analyses were performed to evaluate the hydration kinetics of slag-cement pastes with and without the accelerators ACX and ACN at 20°C and 5°C. The paste mixtures were prepared with a water-to-binder (W/B) ratio of 50% using two binder compositions, N100 and N60. The accelerators were added at a dosage of 4.0% by binder weight (B × 4.0%). Heat release rates were monitored under controlled conditions at each temperature to assess the influence of the accelerators and ambient curing temperature on the hydration behaviour of the slag-cement pastes.

3 RESULTS

3.1 Performance in {N + Slag} concrete

Table 4 shows the fresh properties of slag concrete mixed using N cement with and without hardening accelerators – ACX and ACN, including setting time. Batch name of each mix denotes type of mix as named in table 3, the hardening accelerator, and its dosage in (B × %), in that order.

Table 4 Fresh properties and Setting time in N

Batch Name	SP (B×%)	Slump (cm.)	Air (%)	C.T (°C)	Setting time (hh:mm)	
					Initial	Final
N100– No AC	0.80	19.0	1.3	21	4:25	6:05
N100– ACX – 4.0	0.55	19.0	1.3	21	2:20	3:25
N100– ACN – 4.0	0.90	18.5	1.5	21	3:00	4:10
N60– No AC	0.70	17.5	2.0	21	4:30	6:40
N60– ACX – 4.0	0.50	18.5	1.8	20	2:50	4:30
N60– ACN – 4.0	0.80	19.0	1.3	21	2:55	4:50
N30– No AC	0.65	17.5	1.6	21	4:00	7:00
N30– ACX – 4.0	0.40	18.5	1.8	20	3:00	6:05
N30– ACN – 4.0	0.70	18.0	1.5	21	3:15	5:50

Figs., 3 and 4 show the compressive strength development with time under steam curing and standard curing respectively. In N100, N60, N30 mixes, 4.0% of both ACX and ACN provided almost identical increase in 7 hr. and 18 hr. strength under steam curing at respective temperatures. This increase in early strength didn't influence long-term i.e., 14d. strength. Same trend can be seen in mixes under standard curing as well – using ACX and ACN increased 24 hr., strength without lowering 28d. strength.

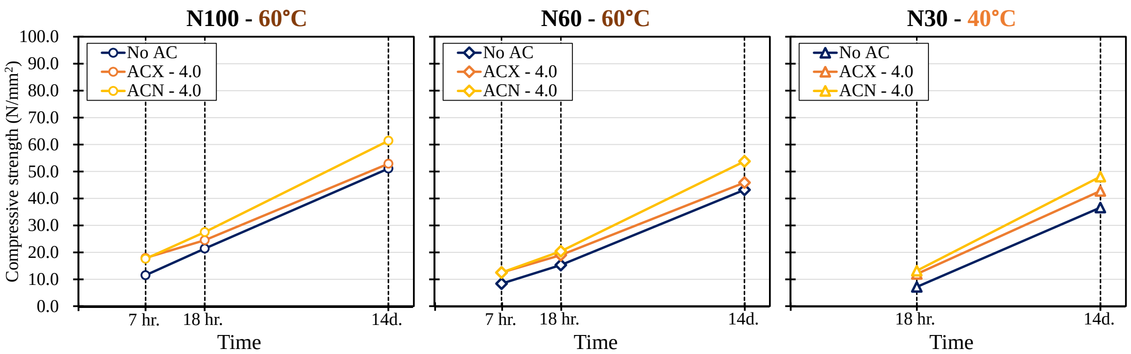

Fig. 3 Compressive strength with time under ***steam curing*** in slag concrete mixes with **N** cement

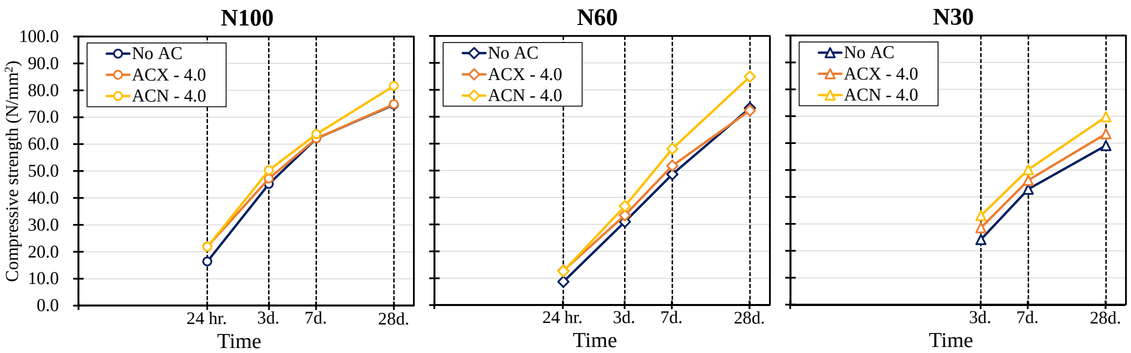

Fig. 4 Compressive strength with time under ***standard curing*** in slag concrete mixes with **N** cement

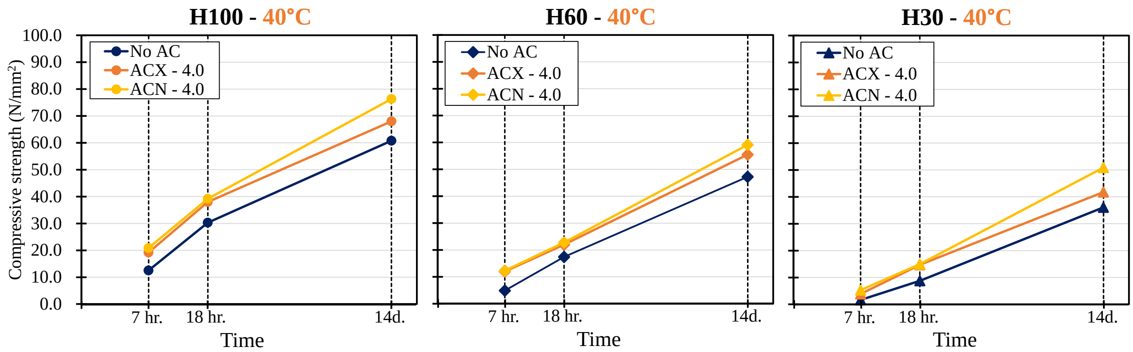

Fig. 5 Compressive strength with time under ***steam curing*** in slag concrete mixes with **H** cement

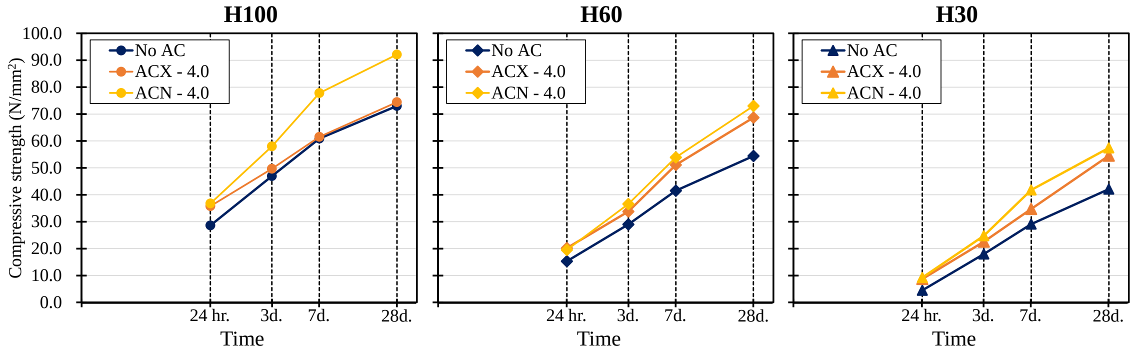

Fig. 6 Compressive strength with time under ***standard curing*** in slag concrete mixes with **H** cement

3.2 Performance in {H + Slag} concrete

Table 5 shows fresh properties of slag concrete mixed using H cement with and without hardening accelerators – ACX and ACN, including the setting time. Batch name denotes the same as described in 3.1.

Figs., 5 and 6 show the compressive strength development with time in slag concretes with H cement under steam curing and standard curing respectively. In H100, H60, H30 mixes, 4.0% of both ACX and ACN provided almost identical increase in 7 hr. and 18 hr. strength under steam curing at 40°C. Using ACX or ACN marginally improved the 14d. long term strength compared to that of no accelerator. Same trend can be seen under standard curing as well – using ACX and ACN slightly increased 24 hr., strength and significantly increased the 28d. strength.

3.3 Performance of ACX and ACN in slag concrete with N vs. H cements

(1) Demoulding time

A minimum compressive strength of 12.0 N/mm² is required for the demoulding of precast concrete. To evaluate the influence of slag replacement and curing conditions, the time to reach this demoulding strength was estimated from the strength development trends shown in Figs. 3–6. Since the compressive strength over time plotted on a logarithmic scale exhibited an approximately linear relationship, a first-order approximation using the least-squares method was applied. The optimal regression parameters obtained were then used to calculate the demoulding time by substituting a target strength of 12.0 N/mm².

The estimated demoulding times were plotted against slag replacement volume, as shown in Fig. 7

Table 5 Fresh properties and Setting time in H

Batch Name	SP (B×%)	Slump (cm.)	Air (%)	C.T (°C)	Setting time (hh:mm) Initial	Final
H100–No AC	0.95	19.0	1.3	20	4:00	5:25
H100–ACX – 4.0	0.75	18.5	1.6	20	2:00	3:00
H100–ACN – 4.0	0.95	19.0	1.4	20	1:35	2:25
H60–No AC	0.75	19.0	1.4	20	4:05	5:55
H60–ACX – 4.0	0.60	19.0	1.2	20	2:25	3:30
H60–ACN – 4.0	0.75	18.0	1.2	20	2:00	3:10
H30–No AC	0.65	18.0	1.1	20	4:25	7:20
H30–ACX – 4.0	0.45	18.5	0.8	20	3:05	5:40
H30–ACN – 4.0	0.75	18.5	1.1	20	2:40	4:15

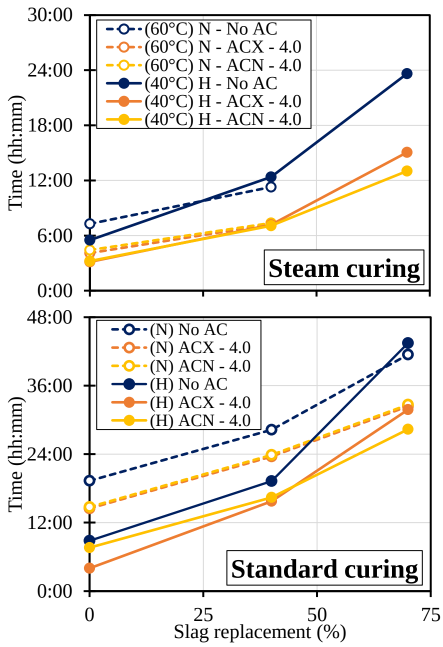

Fig.7 Demolding time in slag concretes

Under steam curing conditions, H100 and H60 mixes without accelerators at 40°C curing exhibited demoulding times comparable to those of N mixes cured at 60°C. This indicates that slag concretes with H cement, despite the lower curing temperature, can match those with N cements in terms of achieving demoulding strength under steam curing. When ACX or ACN was used, demoulding times were further reduced significantly for both N and H cements.

Under 20°C standard curing, slag concretes with H cements surpassed those with N cements in achieving faster demoulding times at almost all slag replacement levels. At 70% slag replacement, the demoulding time for both N and H slag concretes were equal. This indicates that, under standard curing conditions, slag concretes prepared with H cements demonstrate the potential for faster demoulding times compared to those with N cements.

In terms of setting time, slag concretes with H cements generally set faster than those with N cements. However, the impact of using accelerators (ACX or ACN) was more significant than the difference caused by changing cement types.

(2) Impact on long-term strength

Fig. 8 displays the long-term strengths under steam curing (14d.) and standard curing (28d.) of slag concretes relative to the respective strengths of N100 without accelerator under steam and standard curing.

Under steam curing, H100 mixes without accelerator at 40°C achieved higher strength than N100 mixes without accelerator at 60°C. Strength of H60 mixes with ACX or ACN at 40°C surpassed that of N60 mixes with the same accelerators at 60°C. H30 and N30 mixes with ACX or ACN at 40°C achieved similar strength which is approximately 80% of the strength of N100 mixes without accelerators at 60°C.

Under standard curing, N60 and H60 mixes with ACX or ACN achieved strengths > 90% of that of N100 or H100 mix with no accelerators. In contrast, N30 and H30 mixes with accelerators recovered ~ 85% and ~ 75% of the strength of N100 mix, respectively.

The impact of slag replacement on long-term

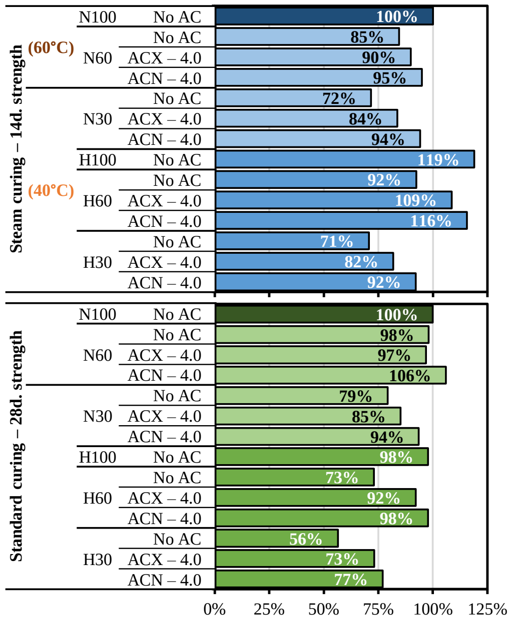

Fig. 8 Long-term strength of slag concretes

strength was more pronounced in concrete made with H cement compared to N cement, under both steam and standard curing conditions. Without accelerators, replacing N cement with 40% and 70% slag resulted in strength losses of 0–15% and 20–30%, respectively. In contrast, the same replacement levels in H cement caused higher strength losses, ranging from 20–25% at 40% slag replacement to 40–45% at 70% replacement. However, the use of accelerators ACX, ACN significantly mitigated these losses in H cement mixes, reducing them to 0–10% and 20–30% for 40% and 70% slag replacement, respectively. This highlights the effectiveness of accelerators in maintaining long-term strength in slag concretes, especially with H cement.

3.4 Effect of temperature on strength development in {H + Slag} concrete

Fig. 9 shows the influence of pre- and post-curing temperature on the 7 hr., strength of H100, H60 mixes; and 18 hr., strength of H100, H60 and H30 mixes - with and without ACX, ACN.

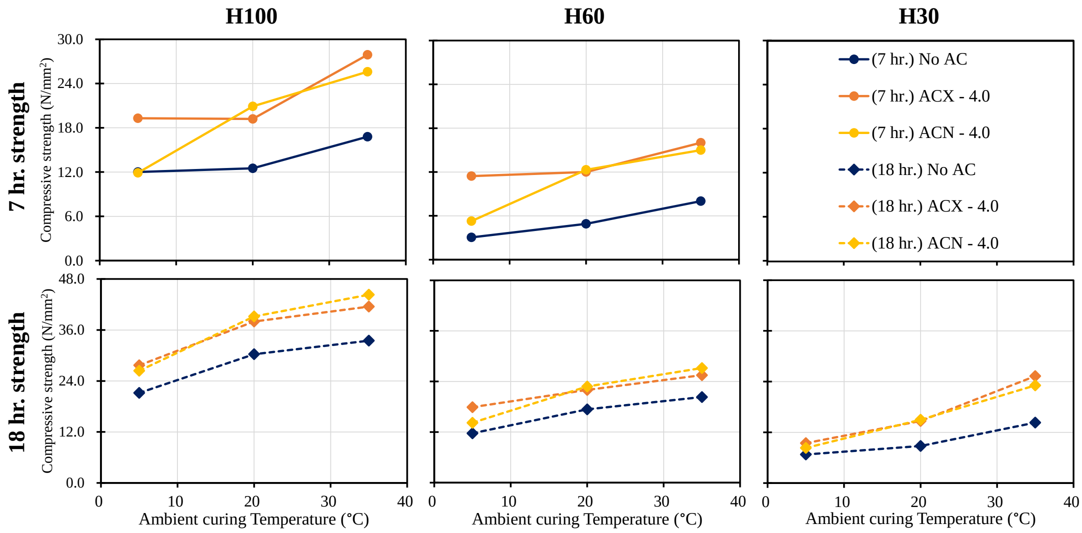

Fig. 9 Effect of ambient temperature on ***steam cured*** strength in slag concrete mixes with **H** cement

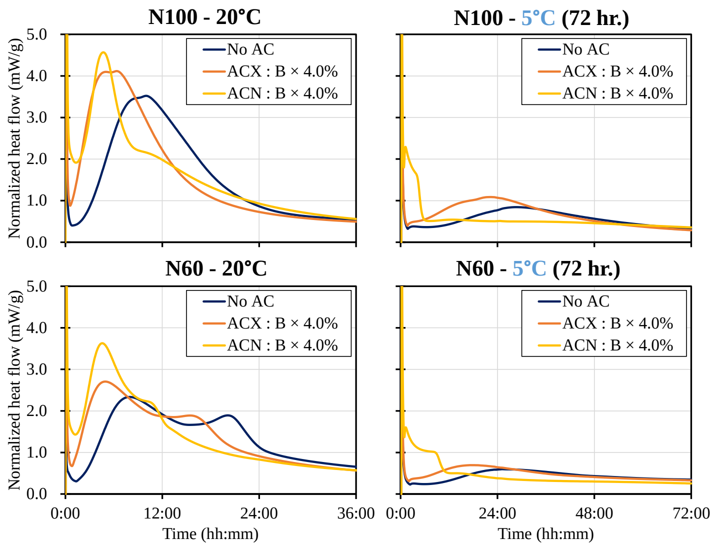

Fig. 10 Isothermal Calorimeter Results for N100, N60 (W/B = 50%) at 20°C and 5°C

When using 4.0% ACX, strength enhancement was uniform across H100, H60 and H30 mixes at 7 hr., and 18 hr., irrespective of the curing temperature. This indicates that the action mechanism of ACX, which involves nucleation and seeding of hydration products, is independent of temperature, making it a reliable accelerator for early-age strength development under varying thermal conditions.

In contrast, the effect of 4.0% ACN exhibited variation depending on curing temperature. At 18 hr., ACN provided strength enhancement like ACX across H100, H60 and H30 mixes. However, at 7 hrs., ACN did not provide any strength enhancement in H100 and H60 mixes. This suggests that action mechanism of ACN, could involve reactions sensitive to temperature and thus, is less effective as accelerator at early ages, particularly under low temperature.

3.5 Calorimeter analysis

The isothermal calorimeter results, shown in Fig. 10, indicate that ACX consistently enhanced the hydration rate in both N100 and N60 cement pastes at 5°C and 20°C, achieving distinct exothermic rate peaks when compared to mixes without accelerators. At 20°C, 4.0% ACN also demonstrated effective acceleration, with its exothermic rate peaks occurring earlier and comparable to those of ACX. However, at 5°C, ACN showed an initial exothermic rate peak followed by a pronounced dormant period, indicating a divergence in its action mechanism under low-temperature condition.

4 CONCLUSIONS

(1) C-S-H seeding based ACX provided comparable strength enhancement to nitrate/nitrite based ACN in slag concrete mixes with N and H cements under steam and standard curing.

(2) Slag concretes with H cement produced early age strength comparable to those with N cement, even at lower curing temperature enabling faster demolding times, even faster with the use of accelerators ACX, ACN. Use of accelerators can mitigate the strength loss on long-term strength. These findings highlight the potential of H cement and slag blends to further reduce CO_2 emissions in precast applications.

(3) ACX provided consistent strength enhancement in early age strength at all curing temperatures. ACN demonstrated a slower early-age strength development at low ambient curing temperatures.

REFERENCES

[1] Mansell, B et. al. : The impact of accelerating admixtures on blended cement hydration for early age strength enhancement, Concrete Institute of Australia's Biennial National Conference, 2021.

[2] 冨田 悠輔, 崔 希燮, 井上 真澄, 須藤 裕司 : 亜硝酸カルシウムを添加した高炉スラグセメント系材料の収縮ひび割れ特性に関する研究, コンクリート工学年次論文集, Vol. 43, No. 1, pp. 131-136, 2021.

[3] John E et. al. : Nucleation seeding with calcium silicate hydrate – A review, Cement and Concrete Research, vol. 113, pp. 74-85, 2018.

[4] Cuesta, A et. al.: Recent Advances in C-S-H Nucleation Seeding for Improving Cement Performances, Materials, vol. 16, no. 4, p. 1462, 2023.

[5] 井元 晴丈, 小泉 信一, Chandra Kiran VINUKONDA, 島田 昌宜 : C-S-H 系硬化促進剤を使用した高炉水砕スラグ高含有コンクリートの強度発現性に及ぼす養生条件の影響, コンクリート工学年次論文集,Vol. 46, No. 1, pp. 1309-1314, 2024.

[6] Chandra Kiran VINUKONDA, 井元 晴丈, 小泉信一, 三森 耀介, Basic performance of high-volume slag concrete using C-S-H based hardening accelerator -I, in 78th Annual Conference of JSCE , 2023.

[7] 堀尾 哲也 : 高炉スラグ微粉末を用いた高耐久性 PC 構造物,中国地方建設技術開発交流会 (鳥取県会場), 2006.