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2019

Presented at Concrete 2019 Conference, Sydney

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Effect of Rapid-set Binder Containing Various Types of Accelerators on Heat Evolution and Selected Fresh and Hardened Properties of Mortar and Concrete Mixes

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Abstract: Advancements in concrete admixtures over the last decade have led to an increase in the use of high early-strength (HES)-low water-to-binder ratio (w/b) concrete. These concrete mixtures have been widely used in concrete pavement replacement and construction to allow roads to be opened to traffic 6 hours after placement. Rapid-set binders utilizing accelerators are required for quick strength development but increase the heat of hydration resulting in the generation of tensile stresses throughout the concrete structure.

These tensile stresses cause the formation of micro-cracks which increase permeability and compromise the structural integrity of the concrete. The increased occurrence of micro-cracking needs to be balanced with the rapid strength gain and short setting time required for construction. In this paper, an experimental study on the influence of various types of accelerating admixtures on heat of hydration of blended cement pastes was assessed and evaluated against a control paste containing calcium chloride as the accelerator. Moreover, the effectiveness of these admixtures was evaluated on selected fresh and hardened properties of mortar and concrete mixes with fixed w/b ratios of 0.45 and 0.42, respectively, according to the requirements of RMS 3201 specification [1].

1 Introduction

The repair of concrete pavements has become increasingly time sensitive as growth in population has resulted in an increase in residential areas further away from business districts meaning once quieter roads are now relied on by an increasing number of commuters. There is an impetus on councils to return roads to service in the minimum amount of time possible. The increased rate of deterioration observed in pavements has led to an increase in the number and type of systems available for the rapid repair and rehabilitation of concrete pavements. Whilst typical ordinary Portland cement (OPC) mixes are suitable for the construction of new pavements as there is no requirement to open the work to traffic within a short period of time, alternative materials with a short setting time are required for repairs to existing roads and bridge decks. It can be difficult to orchestrate repairs, especially in densely populated areas, as the closure of lanes or entire roads results in costs due to traffic delays and permission to do so can be hard to obtain [2]. Therefore, rapid early strength materials for fast-track concrete repair are routinely specified by road authorities.

There are many cementitious preparations available for the maintenance of concrete pavements. Examples include High Early Strength (HES) cement, accelerators, alkali activated slag or Fly Ash (FA), calcium aluminate and calcium sulfoaluminate cements, polymer (e.g. latex) modified cements and prepackaged proprietary blends [3, 4]. However, adding an accelerator to normal concrete on site is more convenient, and familiar. There are a range of chemicals known to accelerate cement hydration such as: calcium chloride (CaCl_2), lithium salts, nitrates, nitrites, thiocyanates, carboxylic acids, hydroxycarboxylic acids, alkanol amines, sodium silicate, aluminates and alkali carbonates. CaCl_2 is among the most tested and well understood accelerators available with the added advantage of being low in cost and is considered in this paper as a baseline. It improves early strength by increasing the rate of reaction of alite and decreases setting time by enhancing the reaction of C_3A [5]. Currently, there are limitations on the use of CaCl_2 in concrete mixes as it accelerates the corrosion of steel tie bars, reinforcement and dowels, can adversely affect shrinkage and cause cracking [1]. Accelerators which do not contain chlorides are numerous, but these alternatives must be tested to ensure they provide an equivalent level of performance. According to RMS 3201 – concrete supply for maintenance [1], typical strength requirements for accelerated concrete mixes are compressive strength of greater than 5 MPa at 6 hours and 40 MPa at 28 days with w/b ratio less than 0.45. In this paper, a range of commercially available accelerators have been investigated with the aim of assessing their suitability for use in rapid setting concrete mixes for the repair of concrete pavements.

2 Experimental programs

2.1 Material properties

2.1.1 Cementitious materials

A Shrinkage Limited (SL) cement was used for all mixes in this study. The mixes also contain fly ash at a replacement level of 10%. Physical properties and chemical composition of cementitious materials are shown in Table 1 and Table 2 respectively.

Table 1. Physical properties of cementitious materials

Materials	Median Particle Size (μm)	Specific Gravity (S.G)	Passing 45 μm sieve (%)	28-day strength index	Fineness index (m^2/kg)
SL Cement	16.3	3.10	94	100	395
Fly ash	13.2	2.10	89	94	370

Table 2. Chemical composition of cementitious materials

Materials	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O _{eq}
SL Cement	63.6	19.0	5.1	2.9	2.8	1.2	0.4
Fly ash	2.5	59.1	28.1	3.7	0.2	0.5	1.4

2.1.2 Aggregate and its grading

Fine sand with specific gravity of 2.59 and water absorption of 0.40%, and manufactured sand with specific gravity of 2.71 and water absorption of 0.8% were used. Coarse aggregate, 20 mm and 10 mm gravel with specific gravity of 2.77 and water absorption of 0.50% were used in all concrete mixes. From Table 3, all coarse and fine aggregates complied with requirements of the specification range listed in AS 2578.1 [6].

Table 3. Grading of coarse and fine aggregates

Coarse Aggregate			Fine Aggregate		
Sieve Size	20 mm	10 mm	Sieve Size	Manufactured Medium sand	Fine Sand
mm	Passing, %		mm	Passing, %	
19.00	98	100	4.75	99	100
13.20	52	100	2.36	83	100
9.50	11	89	1.18	58	100
4.75	1	18	0.600	40	98
2.36	1	4	0.300	25	47
1.18	0	3	0.150	14	2
			0.075	9	0

2.1.3 Admixtures

In this paper, a range of commercially available accelerators have been tested to assess their suitability for use in rapid setting concrete for the repair of concrete pavements. These admixtures contain mixtures of calcium chloride, calcium nitrate and other nitrates, sodium thiocyanate, alkanolamines, organic acids and other inorganic compounds as shown in Table 4.

Table 4. Classes of accelerators present in tested admixtures

Admixture	CaCl ₂	Nitrates	Nitrites	Thiocyanates	Alkanolamines	Organic Acids	Other
A	✓						
B		✓		✓	✓		
C		✓	✓	✓	✓		
D		✓		✓		✓	
E		✓		✓	✓		
F		✓		✓			✓
G		✓		✓			

2.2 Mix proportions

A cement replacement level of 10% by mass with fly ash was maintained throughout the investigation. All blended cement paste and mortar mixes were prepared with fixed w/b of 0.45 with varying accelerator dosages in accordance with their manufacturer's recommendations as shown in Table 5. Concretes were made with a w/b of 0.42 and admixture dosages were in proportion with those used for mortar testing (Table 6).

Table 5. Mortar mix proportions

Materials	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7	Mix 8
SL Cement (g)	405	405	405	405	405	405	405	405
Fly ash (g)	45	45	45	45	45	45	45	45
Sand (g)	1350	1350	1350	1350	1350	1350	1350	1350
w/b	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Admixture A (mL)	18	-	-	-	-	-	-	-
Admixture B (mL)	-	12.5	-	-	-	-	-	-
Admixture C (mL)	-	-	20	-	-	-	-	-
Admixture D (mL)	-	-	-	18	-	-	-	-
Admixture E (mL)	-	-	-	-	10	-	-	-
Admixture F (mL)	-	-	-	-	-	20	-	20
Admixture G (mL)	-	-	-	-	-	-	33	10

Table 6. Concrete mix proportions

Materials	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
SL Cement (kg/m ³)	450	450	450	450	450
Fly ash (kg/m ³)	50	50	50	50	50
Coarse aggregate (kg/m ³)	1080	1080	1080	1080	1080
Fine Aggregate (kg/m ³)	620	620	620	620	620
w/b	0.42	0.42	0.42	0.42	0.42
Admixture A (mL)	18000	-	-	-	-
Admixture B (mL)	-	12500	-	-	-
Admixture C (mL)	-	-	20000	-	-
Admixture D (mL)	-	-	-	20000	-
Admixture E (mL)	-	-	-	-	10000

2.3 Casting, curing and testing of specimens

The heat of hydration of blended cement pastes was determined using a TAM Air 8 channel isothermal calorimeter in accordance with ASTM C1679 [7]. Mixing of cement paste samples was performed externally to the calorimeter using a domestic mixer. Paste was transferred to a glass vial and sealed before insertion into the calorimeter. Heat evolution was monitored for 48 h.

The flow of fresh mortars was evaluated immediately after mixing in accordance with the AS 2701 [8]. Compressive strength prisms were cast with reference to AS 2350.12 and tested at 4 h, 6 h, 24 h, 7 days, and 28 days in accordance with AS 2350.11 [9]. Specimens were stored in saturated lime water with the exception of specimens tested at 4 and 6 h which were stored at 23 °C and ambient humidity.

The plastic properties of fresh concrete (slump, air content, and fresh density) were evaluated in accordance with AS 1012.3.1, AS 1012.4.2, and AS 1012.5 [10-12]. Concrete cylinders of 100 mm in diameter and 200 mm in height were cast for compressive strength testing. The compressive strength of concrete cylinders was tested at 4 h, 6 h, 24 h, 7 days, and 28 days in accordance with AS 1012.9 [13]. Specimens were stored in saturated lime water.

2.4 Results and discussion

2.4.1 Isothermal calorimetry analysis

Early cement hydration reactions can be broken down into five stages (Figure 1) as reported by several researchers [14, 15]:

- (I) the initial stage: immediately within the first few minutes of mixing cement with water, the aluminate phase reacts with water and sulfate, forming a gel-like material (ettringite) surrounding the cement grains. This reaction releases a significant amount of heat and is represented by the first peak of the hydration process;
- (II) The dormancy stage: there is a dormant stage for about two to four hours after mixing in which the reaction of the aluminate phase is controlled by the amount of ettringite gel surrounding the cement grains which limits the access of water to the cement grains, controlling the rate of the aluminate reaction. This stage is characterized by minimal release of heat;
- (III) The acceleration stage: the pore solution becomes super-saturated with calcium ions, mainly from dissolving alite and belite, fibre-like calcium silicate hydrate (C-S-H) gel and crystalline calcium hydroxide (C-H) start to form causing significant heat evolution. The acceleration stage is represented by the second peak of hydration;
- (IV) The deceleration stage: interaction of C-S-H gel and crystalline C-H with remaining water and undissolved cement grains slows down the alite reaction, reducing the heat of hydration. The amount of sulfate starts to deplete and thus the remaining aluminate reacts with ettringite to form monosulphate. The formation of monosulphate generates some heat, which may be associated with the third hydration peak;
- (V) The slow continued reaction stage: belite dissolves and releases calcium ions very slowly and starts to produce C-S-H and C-H after several days. However, as long as alite and belite remain in the cement system and there is enough water available in the system, the silicates will continue to hydrate.

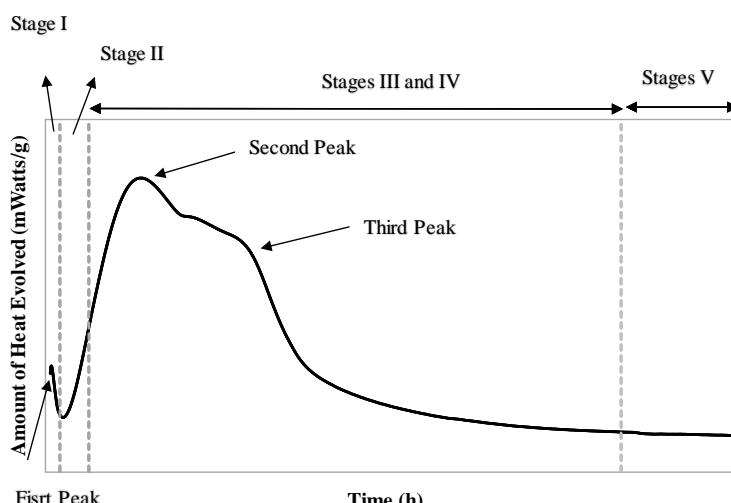


Figure 1: Common cement heat evolution curve [15]

Figure 2 shows the heat evolution of the blended cement pastes containing various dosages of accelerators with fixed w/b ratio of 0.45. It can be seen that all mixes containing non-chloride accelerators experienced all five stages mentioned above specifically second peak of hydration while it did not happen in traditional mix 1 which contains calcium chloride as an accelerator.

The peak due to the acceleration stage is correlated to the early strength of mortars (see Figure 4) for mixes 1 – 7. The maximum of this peak occurs in the following order from earliest to latest: 1, 7, 2 = 4, 6, 5 and 3. It can be seen in Figure 4 that the 4 and 6 h strengths of mortars decrease in the same order indicating the effectiveness of these admixtures at accelerating the reaction of alite at the dose rates suggested by the manufacturers. Mix 8, which contains a mixture of admixtures F and G, does not fit this pattern, however. The timing of the maximum of the alite reaction peak would indicate its early strength should lie somewhere between that of mixes 7 and 2 + 4. Instead, mix 8 attains a higher strength than the other mixes at 4 and 6 h. It is likely that admixture G promotes strength gain by means other than a rapid acceleration of the reaction of alite.

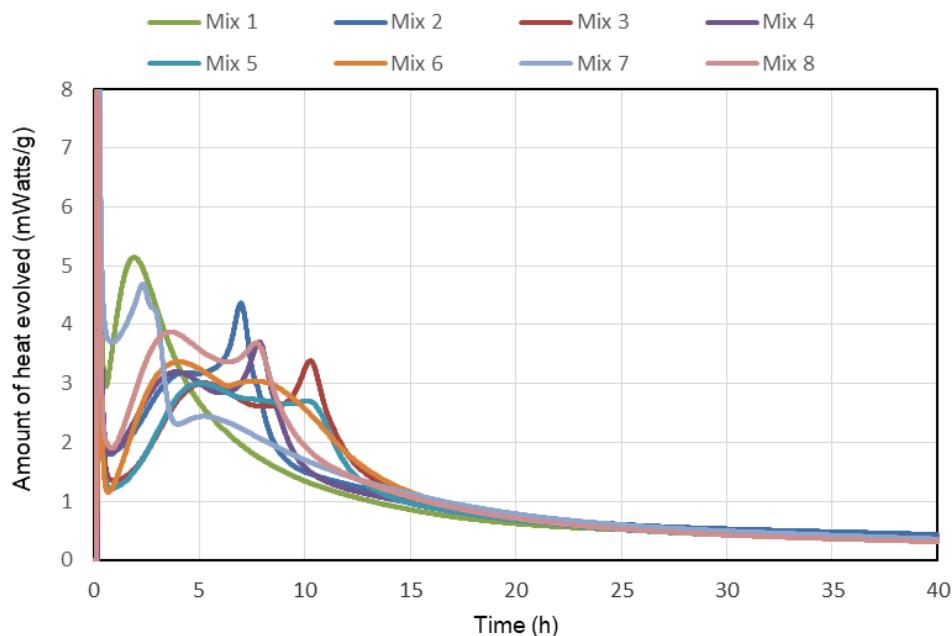


Figure 2. Heat evolution curve for blended pastes

2.4.2 Plastic properties

Mortar flow was tested up to 40 minutes after mixing as shown in Figure 3. It can be seen that mix 8 performed favourably, having a high initial flow that decreased steadily over 40 minutes. Mixes 2 and 4 behaved similarly; despite having a lower initial flow a steady decrease was observed over time. In addition, the plastic properties of tested concrete mixes are presented in Table 7.

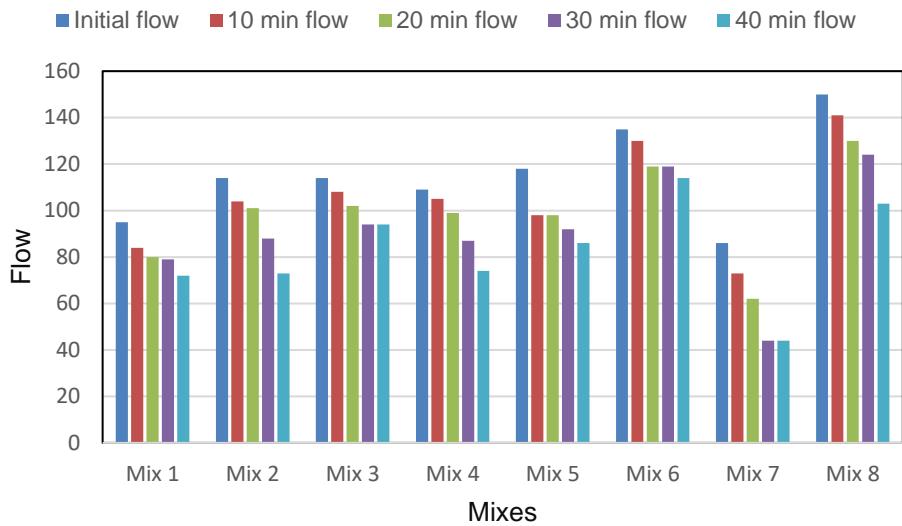


Figure 3. Slump retention of mortar mixes

Table 7: Plastic properties of concrete mixes

Concrete Mix	w/b	Slump(mm)		Air Content (%)	Fresh Density (kg/m ³)
		Before adding accelerator	After adding accelerator		
Mix 1	0.42	60	105	1.5	2385
Mix 2	0.42	60	95	1.6	2400
Mix 3	0.42	70	120	1.3	2395
Mix 4	0.42	75	110	1.4	2390
Mix 5	0.42	65	120	1.4	2405

2.4.3 Strength properties

The 4 and 6 h strengths of mortar bars are presented in Figure 4 and show the trend in early strength. Mix 3 was found to attain the lowest strength followed by mix 5, mix 6, mixes 2 and 4, mix 7, mix 1 and mix 8. This order is consistent with results observed from calorimetry data (see Section 2.4.1). The effect of the accelerators on 28 d strength is varied with strengths ranging from 66 – 76 MPa as shown in Figure 5.

It can also be seen from the concrete strength results as shown in Figure 6 that concretes with a higher early strength, such as mix 4, tended to attain lower ultimate strengths. Mixes 1, 2 and 4 reached satisfactory strengths at 6 h whilst mixes 1 – 5 all reached 40 MPa at 28 days in accordance with RMS 3201. According to the results, it seems the possible increases in admixture dosages or changing their chemical compositions might be necessary to allow all mixes to achieve the strength required by RMS 3201 for use in the repair of concrete pavement.

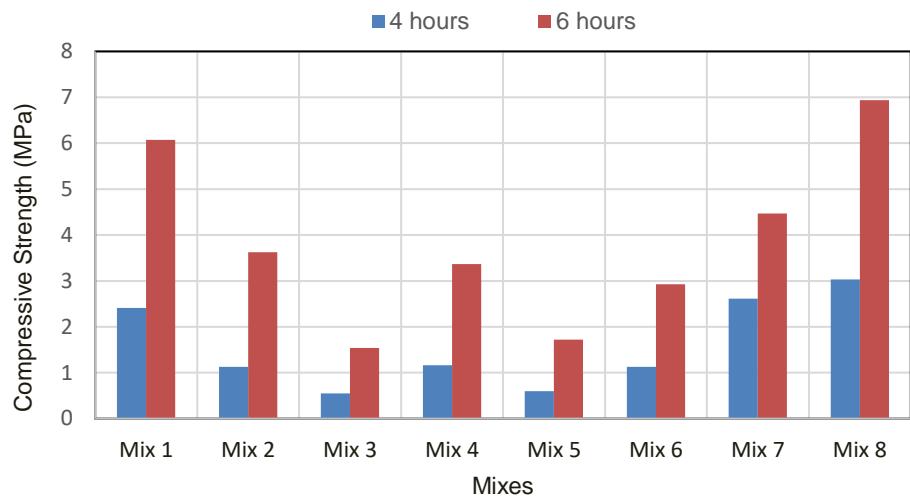


Figure 4: 4 and 6 hour compressive strength of mortar mixes

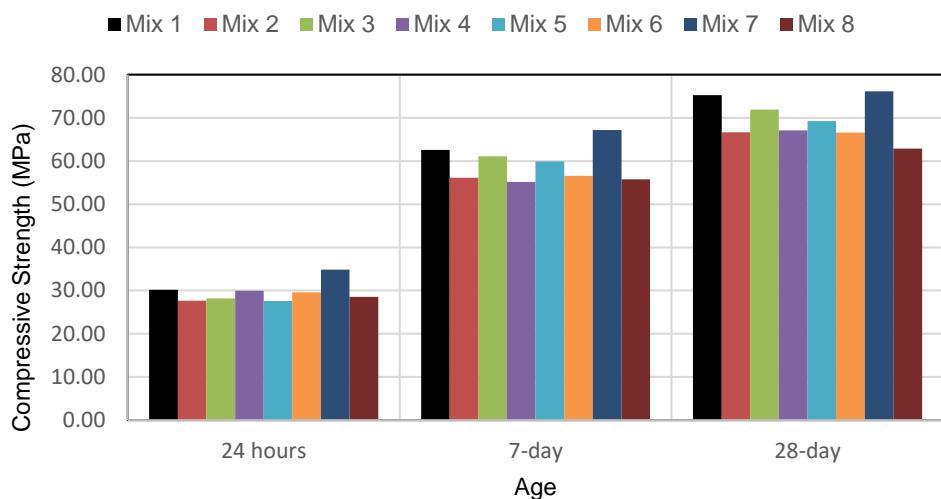


Figure 5: 24h, 7d and 28d compressive strength of mortar mixes

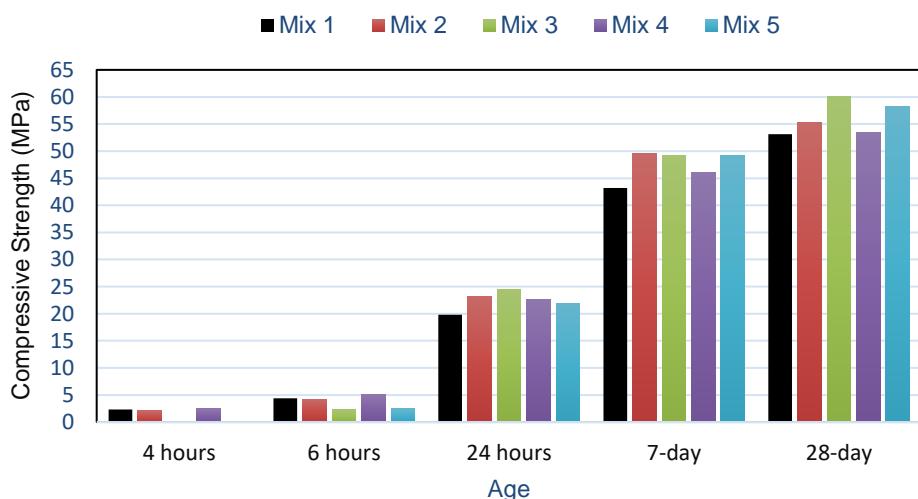


Figure 6: Compressive strength of concrete mixes up to 28 days

3 Conclusions

On the basis of the results obtained from this research work, it can be concluded that it is possible to make rapid set concrete suitable for the repair of concrete pavement using commercially available accelerators without CaCL₂. More work is required to confirm the correct dosage of accelerators to achieve the requirement of RMS 3201 specification of 5 MPa at 6 h. The effect of accelerators on the hydration of cementitious materials was observed using calorimetry and the results were consistent with the early strength data obtained from mortar bar testing.

4 Acknowledgements

The authors gratefully acknowledge the support of Boral Cement and approval to publish this article. The opinions expressed are entirely those of the authors and not necessarily the policies and practices of the organizations they represent.

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