THE ROLE OF NA_2O_{EQ} RATIO ON THE FLOWABILITY AND STRENGTH DEVELOPMENT OF CEMENTITIOUS SYSTEMS IN THE PRESENCE OF A POLYCARBOXYLATE ETHER-BASED ADMIXTURE

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ABSTRACT

In this study, the effect of equivalent Na_2O (Na_2O_{eq}) ratio of cement on fresh properties and compressive strength of paste and mortar mixtures containing polycarboxylate ether-based high range water reducing (HRWR) admixture was investigated. A low and a high alkali cement were used. Five mixtures having five different Na_2O_{eq} ratios were prepared with increasing alkali content of the cement by incorporating three different amounts of NaOH solution to the low alkali cement-bearing mixtures. Irrespective of the absence or presence of HRWR, Na_2O_{eq} content of the mixtures was found to have a considerable adverse effect on the fresh properties of the mixtures, particularly on their flow loss. NaOH addition increased 1-day compressive strength of the mortar mixtures, however, reduced the compressive strength at later ages. In spite of having a lower fineness and a longer setting time, low alkali cement showed slightly higher 1-day strength than high alkali cement. This seems to have occurred, to some extent, from the higher HRWR admixture demand (0.4 wt.%) of the high alkali cement-bearing mixture than that of the mix containing low alkali cement (0.25 wt.%). At later ages, both of the cements showed equivalent strength values.

KEYWORDS

alkali content of cement, fresh properties, cement paste, mortar mixture

INTRODUCTION

Concrete quality is controlled by the flow behavior of cement paste, which is related to the dispersion of cement particles. HRWR admixtures provide a better dispersion of cement particles, thereby, producing paste of a higher fluidity. With the development of high strength/high performance concrete, HRWR has become indispensable. These admixtures are adsorbed on the cement particles. This adsorption is uneven and depends on the clinker composition of cement and the type of admixture [1–3].

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It is well known that, polycarboxylate-based water reducing admixtures are more effective than normal water reducing admixtures (WRA) due to their steric effect [3]. This makes it possible to reduce the water requirement of the mixture significantly for a given workability. Therefore, at a given water/cement ratio (w/c), it is possible to reduce cement content without harming strength or workability [4]. However, for the production of 1 ton of cement roughly 1.2 tons of raw materials and about 130 kWh energy are required. Furthermore, roughly 1-ton CO_2 will also be emitted. The importance of cement saving in concrete becomes more evident regarding the above-mentioned figures [5]. Furthermore, for a given workability, WRA may be used to improve the strength of concrete by reducing its w/c ratio [6]. This provides reduction in the cross-section of reinforced concrete structural elements. Accordingly, the cost of the concrete member can be reduced. However, WRAs may show incompatibility with some cements, which may result in some adverse side effects in cementitious systems such as early stiffening, set retardation, loss of workability, segregation, increasing risk of bleeding and shrinkage [7–10]. Therefore, selection of a compatible WRA for any cement is a must. This makes it possible to achieve required mixture characteristics with less cement and less WRA, since the efficiency of the WRA will be increased by selecting a compatible cement-admixture couple. There are several studies on the cement-admixture compatibility in the literature. The complex cement-admixture compatibility has become even more complicated by increasing the types of cement and admixture [2, 3, 11]. Therefore, there is still no broadly-accepted conclusion on the subject. The soluble-alkali content of the cement is one of the factors affecting workability and consistency of the cementitious systems. The performance of HRWR admixture in the cementitious systems depends on the type of admixture and cement. The fineness of cement, amount and type of C_3A, soluble-alkali content, type and amount of calcium sulfate, as well as free CaO content are the cement-related factors affecting the cement-admixture compatibility. The chemical structure of the polymer, the types of bonds between molecules, molecular weight of the admixture, the degree of sulfonation, admixture content and the method of its addition into the mixture are the admixture-related factors affecting the cement-admixture compatibility [12–21]. It is reported that the fresh and rheological properties of the cementitious systems improve by decreasing the alkali content of cement [22–24]. This is due to improved reactivity of the C_3A compound in high alkaline medium, which increases the rate of calcium sulfoaluminate hydrates formation. Some studies that investigate the effect of alkali content of cement on the properties of cementitious systems are summarized below.

The effect of soluble alkalis on the cement-polynaphthalene sulfonate superplasticizer compatibility during the first few minutes of hydration was investigated by Shiping et al. [25]. Test results demonstrated that the soluble-alkalis, entering into the pore solution during the first few minutes, were the key parameter in controlling fluidity and fluidity loss of the cementitious systems containing WRA. Irrespective of admixture dosages and cement type, the optimum soluble-alkali content for increasing initial fluidity and decreasing time-dependent fluidity loss was found to be on the order of 0.4%–0.5% Na_2O_{eq}. Besides, the C_3A content had practically no effect on the fluidity loss of paste containing cement with an optimum amount of soluble alkalis.

Dils et al., [26] investigated the effect of the different cement types, having low C_3A content and moderate Blaine fineness, on the workability, rheology and compressive strength of mortar mixture containing polycarboxylate ether-based high range water reducing admixture. Test results showed that the microstructure was influenced by the chemical composition of cement, and by the workability of the mixture. It was reported that cement with a higher

C_3A and alkali content as well as a higher fineness, but a lower content of SO_3 gave the lowest performance in terms of fresh properties.

The effect of alkali sulfate content of cement on the rheological behavior of cement paste containing SP was studied by Nawa et al., [1]. In order to measure the rheological parameters a rotational viscometer was used. Authors stated that a larger amount of HRWR admixture was rapidly adsorbed on the C_3A and C_4AF compared to that adsorbed on C_3S and C_2S compounds. The presence of alkali sulfate inhibited the adsorption of HRWR admixture on C_3A and C_4AF, permitting increased adsorption on C_3S and C_2S. The reduction of viscosity of cement paste by HRWR admixture was dependent mainly on its adsorption on the C_3S and C_2S. Therefore, an increase in alkali sulfate led to an increase in the adsorption of admixture on the C_3S and C_2S compounds, causing reduction in the viscosity of the paste. An excessive amount of alkali sulfate, however, compressed the electrical double layer, providing an increase in the viscosity of the paste. It was concluded that there was an optimum alkali sulfate level with respect to the fluidity of the cement paste containing HRWR admixture.

The influence of HRWR admixtures and cement types on the fluidity of mortar mixtures having different water/cement (w/c) ratios was investigated by Chandra S, Björnström [27]. For this study, two different types of admixtures i.e., lignosulfonic acid (LS) and melamine sulfonic acid (SMF), and three different types of cement (ordinary portland, low alkali and white cement) were used. Test results showed that LS was more effective than SMF in providing better fluidity. Furthermore, white cement resulted in the highest fluidity among the cements. This was attributed to the lower $C_3A + C_4AF$, lower alkali content and higher SO_3 content of the white cement than the other cements.

In other research, the effects of specific surface area, C_3A, Na_2O_{eq} and SO_3 content of cement, as well as the interaction of these factors on the fresh and rheological properties of mortar mixtures containing polyether- and polycarboxylate-based superplasticizer admixtures, were investigated by Gelaszewski [28]. For this purpose, 19 cements, two polyether-based admixtures, having different molecular weights, and one type polycarboxylate-based admixture were used. The composition and specific surface of those cements were changed greatly according to an assumed research plan, while other properties were kept constant. The cement-based factors that affect fresh properties of mortar mixtures, in order of decreasing severity, were found to be C_3A content, cement fineness and equivalent alkali content. However, no considerable influence of SO_3 content of cement on the fresh properties of mixtures was observed. The performance of HRWR admixture decreased by increasing fineness, C_3A, and alkali content of the cement. Upon increasing the cement fineness, yield stress values of the mixtures increased, however, their plastic viscosity decreased slightly. The effect of C_3A content on the fresh properties of the mortar mixtures was more pronounced upon increasing fineness of cement and its alkali content.

Recently, various research projects related to the effect of cement properties on the fresh and rheological properties of cementitious systems were carried out [29, 30]. However, there is no general agreement on the matter. Furthermore, to the authors knowledge, a study evaluating the effect of alkalis incorporated into the mix by the addition of NaOH on the properties of cementitious systems has not yet been undertaken and published. At present, some tests such as ASTM C1293 (Determination of length change of concrete due to ASR) recommend the addition of NaOH to the mixture, when the total alkali content of cement is less than 1.3%. Since the addition of NaOH to the mixture adversely affects the fresh properties of cementitious systems, especially their flow loss and the permeability of the mixture, then this influences the durability performance and may increase further due to trouble during placing and compacting of the specimens. In this study, the effect of Na_2O_{eq} content on the fresh properties and compressive strength of cement paste and mortar mixtures was investigated. For this project, two CEMI 42.5R type cements having low (0.63%) and high (1.04%) Na_2O_{eq} contents were used. In addition to the cement paste and mortar mixtures prepared with these cements, three mixtures were produced by adding three different amounts of NaOH to the mixture containing low alkali cement. In this way, 5 paste and 5 mortar mixtures having different Na_2O_{eq} contents were studied. The initial and final setting times, Marsh-funnel flow time, mini-slump value and temperature of the paste mixtures were determined. In the mortar mixtures, the admixture requirement for a given flow, time-dependent flow and V-funnel flow as well as 1, 3, 7 and 28-day compressive strength values were obtained.

2. MATERIALS, MIX PREPARATION AND TEST PROCEDURES

2.1 Materials

In this study, two CEMI 42.5R portland cements, conforming with EN 197-1 Standard and having high alkali (HA) and low alkali (LA) contents were used. The Na_2O_{eq} (Na_2O + 0.658 K_2O) contents of the cements were 1.04% and 0.63%, respectively. The chemical composition of the cements, their clinkers and the gypsum rocks used in manufacturing of the cements are shown in Tables 1 and 2, respectively.

TABLE 1. Chemical composition and physical properties of clinkers and cements.

Item (%)	High Alkali (HA)	Low Alkali (LA)
SiO_2	19.72	19.54
Al_2O_3	5.31	4.80
Fe_2O_3	3.37	5.71
CaO	61.33	61.65
MgO	2.33	1.89
SO_3	3.33	3.12
Na_2O	0.53	0.37
K_2O	0.77	0.40
Cl^-	0.0136	0.0087
Insoluble residue	0.48	0.20
Loss of ignition	2.09	1.53
Total	**99.24**	**99.22**
Equivalent alkali ratio (%)	1.04	0.63
Specific gravity	3.08	3.13
Specific surface (Blaine, cm^2/g)	3960	3570
Volume stability (Le Chatelier, mm)	1.00	1.00

TABLE 2. Chemical composition of clinkers and gypsum rocks.

Item (%)	Clinker		The gypsum rocks that added to the clinkers	
	HA	LA	HA	LA
SiO_2	20.91	21.24	0.17	3.48
Al_2O_3	6.85	4.4	0	0.58
Fe_2O_3	2.52	5.25	0.07	0.4
CaO	66.17	65.67	33.01	32.09
MgO	1.23	1.4	1.12	1.36
Na_2O	0.34	0.32	0.46	0.47
K_2O	1.12	0.45	0	0.14
SO_3	0.5	0.45	38.02	38.51
Cl^-	0.008	0.009	—	—
Free CaO	2.05	1.18	22.14	22.85

For the preparation of mortar mixtures, standard sand conforming to EN 206-1 was used. In addition to HA cement- and LA cement-bearing mixtures, three other mixtures having Na_2O_{eq} contents of 0.84%, 1.04% and 1.26% were produced by adding appropriate amounts of NaOH into the mixing water of the LA cement-containing mixture. Hence, 5 cement pastes and 5 mortar mixtures were produced. The mixtures are designated on the basis of cement type (HA or LA), Na_2O_{eq} content and % NaOH added to the mix. For example, the mixture containing LA cement with a Na_2O_{eq} content of 0.63% without any NaOH addition is shown as $LA_{(0.63 + 0)}$. Accordingly, the mixture produced from the same cement and containing 0.21% extra Na_2O_{eq} by NaOH addition is designated as $LA_{(0.63 + 0.21)}$. In either paste or mortar mixtures, a polycarboxylate-ether based HRWR admixture was used. The properties of the admixture given by its manufacturer are shown in Table 3.

2.2 Mix Preparation

For the paste mixtures, w/c ratio, cement content and water content were kept constant as 0.35, 1000 g and 350 g, respectively. For each cement type, in addition to the control mixture

TABLE 3. Some properties of polycarboxylate ether-based high range water reducing admixture.

Type	Alkali content (%) (Na_2O)	Density (g/cm^3)	Solids content (%)	Chloride content (%)	pH, 25 °C
polycarboxylate ether-based high range water reducing admixture	< 5	1.098	35.73	0.012	5.97

containing no water reducing admixture, 8 different paste mixtures were prepared by addition of HRWR admixture ranging from 0.5% to 2.25 wt.% of the cement. However, the control mixture and the mixture containing 0.5% HRWR admixture showed no flow through the Marsh-funnel.

The mortar mixtures were prepared in accordance with the ASTM C 109 Standard. Using different dosages of the HRWR admixture, the w/c ratio, sand/binder ratio and flow value of the mortar mixtures were kept constant as 0.485, 2.75 and 270±10 mm, respectively.

2.3 Test methods

In the cement paste mixtures initial and final setting times, Marsh-funnel flow time and mini slump values were determined. Setting times of 10 cement pastes having 5 different Na_2O_{eq} contents and containing 2 different amounts of HRWR (0% and 0.2 wt.% of cement) were determined according to EN 196-3. Besides, Marsh-funnel and mini-slump tests were carried out in accordance with the methods proposed by Aïtcin [14] and Kantro [31], respectively.

The flow value and the V-funnel flow time of the mortar mixtures were measured in accordance with the ASTM C1437 Standard and EFNARC 2002 recommendations, respectively. Furthermore, in order to investigate the change of flow value and V-funnel flow time of the mortar mixture by elapsing time, these tests were repeated after 15, 30, 45 and 60 minutes from the casting. Besides, 1, 3, 7 and 28-day compressive strengths of the mortar mixtures were determined on 50 mm cube specimens in accordance with the ASTM C 109 Standard.

3. TEST RESULTS AND DISCUSSION

3.1 Fresh state properties

The initial and final setting times of the mortar mixtures (containing 0% or 0.2 wt.% HRWR admixture) are given in Table 4. As noted in Table 4, the initial and final setting times of the NaOH-free $LA_{(0.63 + 0)}$ paste were longer than the other samples. Irrespective of the presence or absence of HRWR admixture, the water requirement for normal consistency increased with the addition of NaOH. The effect was more pronounced with increasing NaOH contents. However, as expected, the water requirement for normal consistency was reduced by the utilization of the HRWR admixture.

As seen from Figure 1-a, the setting time of the paste mixtures decreased with increasing the additions of NaOH. In the absence of HRWR admixture, the initial setting times of the mixtures were reduced by 6 to 32% in comparison to the NaOH-free $LA_{(0.63 + 0)}$ mixture. The corresponding reductions in final setting times were 10 to 42%. As seen from Figure 1-b, for the mixtures containing HRWR admixture, the reductions in the initial and final setting times of the mixtures upon NaOH addition were 9–36% and 18–46%, respectively.

The setting times of the paste mixtures increased by using HRWR admixture. However, in the NaOH containing mixtures, the effect of utilization of HRWR admixture on the setting times of the mixtures was lower than those of the NaOH-free mixtures. In other words, the presence of the NaOH solution in the cementitious system reduced the set retarding effect of the HRWR admixture (Table 4).

The initial and final setting times of NaOH-free $HA_{(1.04 + 0)}$ mixture having a Na_2O_{eq} content of 1.04% were 20% and 15% lower than those of NaOH-free $LA_{(0.63 + 0)}$ mixture, respectively. The higher alkali content and higher fineness of HA cement, compared to those of LA cement, seem to be responsible for this behavior. On the other hand, having same Na_2O_{eq}

TABLE 4. Initial and final setting times of cement paste mixtures.

Paste mixture	Water requirement for normal consistency (%)	Setting time (min)	
		Initial	Final
Cement paste mixtures containing no HRWR admixture			
LA*$_{(0.63 + 0)}$	28.2	190	290
LA$_{(0.63 + 0.21)}$	28.4	178	260
LA$_{(0.63 + 0.41)}$	28.5	149	203
LA$_{(0.63 + 0.63)}$	28.6	129	168
HA**$_{(1.04 + 0)}$	28.5	150	246
Cement paste mixtures containing 0.2% wt of cement HRWR admixture			
LA$_{(0.63 + 0)}$	27.6	220	322
LA$_{(0.63 + 0.21)}$	27.9	201	272
LA$_{(0.63 + 0.41)}$	28.1	167	214
LA$_{(0.63 + 0.63)}$	28.3	140	175
HA$_{(1.04 + 0)}$	28.0	171	266

*low alkali cement, ** high alkali cement

content, HA$_{(1.04 + 0)}$ cement showed a similar initial setting time to that of LA$_{(0.63 + 0.41)}$ cement either in the presence or absence of HRWR. It should be noted that the alkali content of LA$_{(0.63 + 0.41)}$ cement was brought to the intended level by NaOH addition.

Marsh-funnel flow time, mini-slump value and temperature of the paste mixtures containing different amounts of HRWR admixture are given in Table 5. In addition, the Marsh-funnel flow time-admixture dosage relationship of the mixtures is shown in Figure 2. As seen from the results, irrespective of NaOH content, the Marsh-funnel flow times of the mixtures decreased by increasing HRWR admixture content. However, beyond a certain admixture dosage, the flow time of mixtures was not significantly changed. The saturation point is defined as the point at which the difference between the two successive values of the flow times is less than 5 seconds with an increase in the admixture dosage. As seen from Figure 2, the LA$_{(0.63 + 0)}$ mixture showed the lowest Marsh-funnel flow time among the tested mixtures. The saturation point of this mixture was 1%. The corresponding value for the HA$_{(1.04 + 0)}$ mixture was 1.25%, denoting that the saturation point (admixture requirement) increases by increasing the alkali content of cement.

The addition of NaOH up to 0.41 wt.% of cement had no effect on the saturation point of LA$_{(0.63 + 0)}$ mixture. However, the flow times at saturation point of the mixture increased by NaOH addition. The effect was more pronounced at higher inclusion levels. Moreover, the flow time at saturation point of LA$_{(0.63 + 0)}$ was 38% greater than that of LA$_{(0.63 + 0)}$ mixture.

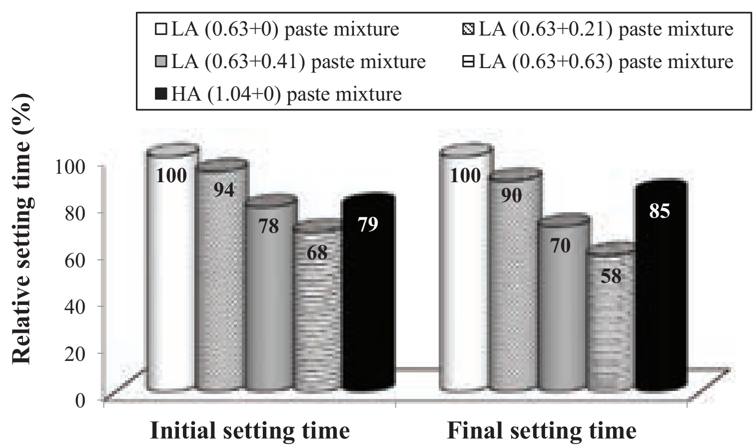
The NaOH-free HA$_{(1.04 + 0)}$ mixture having 1.04% equivalent alkali ratio showed lower performance in terms of saturation point and flow time at saturation point compared to the LA$_{(0.63 + 0.41)}$ mixture. As mentioned earlier, the LA$_{(0.63 + 0.41)}$ mixture was brought to the same equivalent alkali ratio (1.04) with the NaOH-free $HA_{(1.04+0)}$ mixture by adding 0.41% NaOH. Among the mixtures, the $LA_{(0.63+0.63)}$ mixture with the highest NaOH ratio showed the lowest performance in terms of Marsh-funnel flow time.

Regardless of the NaOH content, the mini-slump values of the mixtures increased by increasing the HRWR admixture content up to a certain admixture dosage. However, mini-slump values of the mixtures decreased by increasing NaOH content. As in the Marsh-funnel test, the $LA_{(0.63+0.63)}$ mixture containing the highest amount of NaOH solution showed the lowest performance in terms of flow. The best flow performance was observed in the $LA_{(0.63+0)}$ mixture which was prepared by low alkali cement without any NaOH addition.

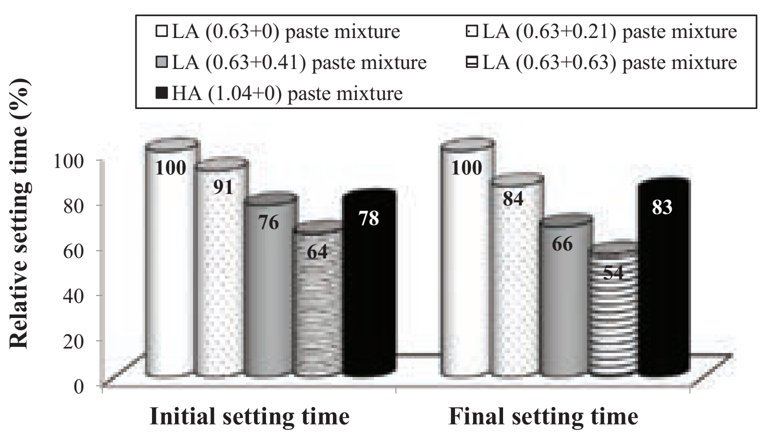
At all admixture dosages, the temperature of the mixtures increased with the addition of NaOH solution. The effect became more pronounced by increasing NaOH content, so that addition of 0.63% NaOH to $LA_{(0.63+0)}$ mixture resulted in 4°C increase in the mixture temperature.

As seen from Figure 3, there is a strong exponential relationship between mini-slump value and Marsh-funnel flow time of the paste mixtures.

FIGURE 1. Initial and final setting times of cement paste, a: mixture containing no HRWR admixture, b: mixture containing 0.2 wt.% of cement HRWR admixture.



(a)



(b)

FIGURE 2. Marsh-funnel flow time of paste mixture depending on the admixture dosage.

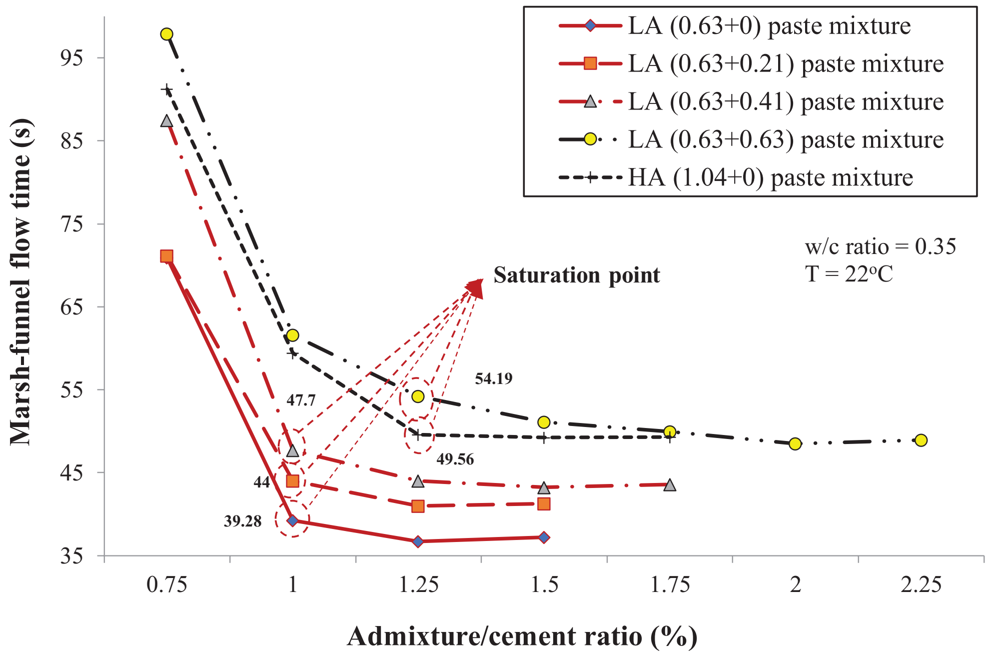
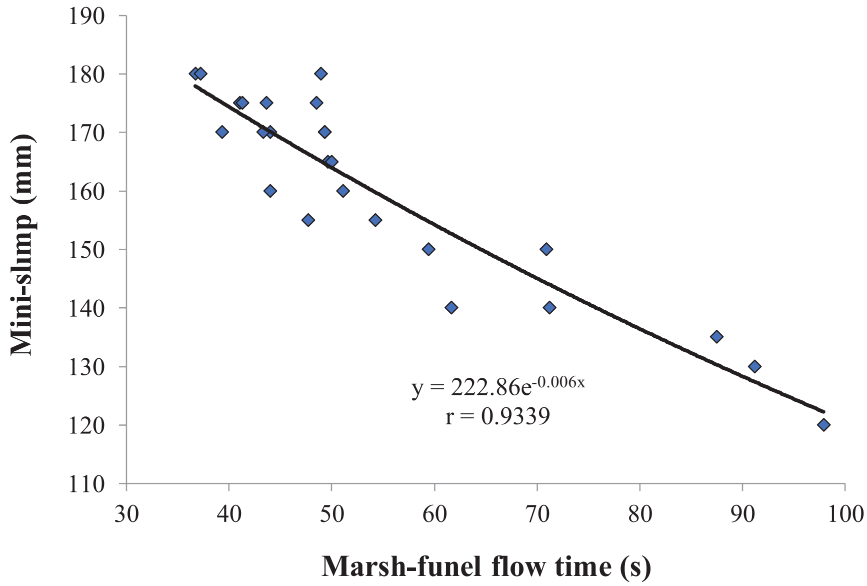


TABLE 5. Marsh-funnel flow time, mini-slump and temperature of cement paste mixtures.

Test	Paste mixtures	0.75	Admixture/cement ratio (%) 1	1.25	1.5	1.75	2	2.25
Marsh-funnel flow time (s)	$LA^{**}_{(0.63+0)}$	70.9	39.3	36.7	37.2	Seg*	Seg*	Seg*
	$LA_{(0.63+0.21)}$	71.2	44	41	41.3	Seg*	Seg*	Seg*
	$LA_{(0.63+0.41)}$	87.5	47.7	44.0	43.3	43.6	Seg*	Seg*
	$LA_{(0.63+0.63)}$	97.9	61.6	54.2	51.1	50	48.5	48.9
	$HA^{***}_{(1.04+0)}$	91.2	59.4	49.6	49.3	49.3	Seg*	Seg*
Mini-slump (mm)	$LA_{(0.63+0)}$	150	170	180	180	Seg*	Seg*	Seg*
	$LA_{(0.63+0.21)}$	140	160	175	175	Seg*	Seg*	Seg*
	$LA_{(0.63+0.41)}$	135	155	170	170	175	Seg*	Seg*
	$LA_{(0.63+0.63)}$	120	140	155	160	165	175	180
	$HA_{(1.04+0)}$	130	150	165	170	170	Seg*	Seg*
Temperature (°C)	$LA_{(0.63+0)}$	25.5	25.3	26	25.5	Seg*	Seg*	Seg*
	$LA_{(0.63+0.21)}$	27	27.1	27.2	26.9	Seg*	Seg*	Seg*
	$LA_{(0.63+0.41)}$	27.4	27.4	27.4	27.1	27.2	Seg*	Seg*
	$LA_{(0.63+0.63)}$	29.5	29.7	29.5	29.7	29.5	29.4	29.9
	$HA_{(1.04+0)}$	27.6	27.9	27.5	27.8	27.6	Seg*	Seg*

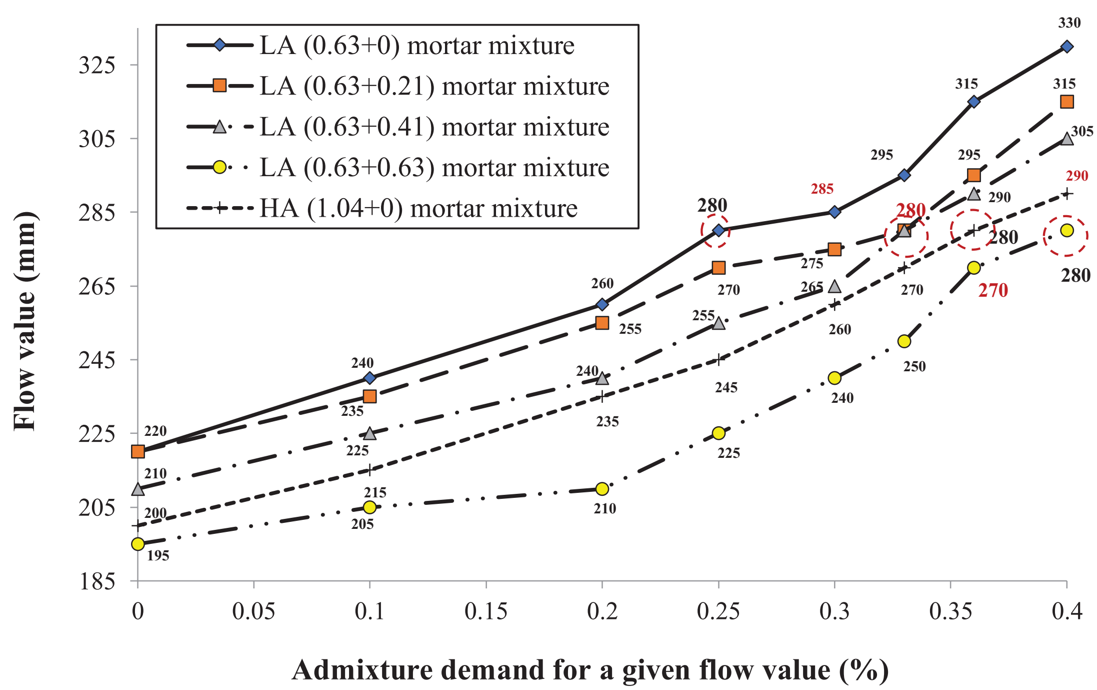
*In the mentioned mixture segregation was observed, **low alkali cement, ***high alkali cement

FIGURE 3. Relationship between mini-slump value and Marsh-funnel flow time of paste mixture.



In order to investigate the effect of Na_2O_{eq} content on the mortar flow value, mixtures having w/c ratio of 0.485, sand/binder ratio of 2.75 and an admixture dosage ranging from 0 to 0.4% (by cement weight) were prepared. As seen from Figure 4, among the mixtures containing no HRWR admixture, $LA_{(0.63 + 0)}$ showed the maximum flow performance. $LA_{(0.63 + 0.63)}$ mortar

FIGURE 4. Flow values of mortar mixture depending on admixture use dosage.

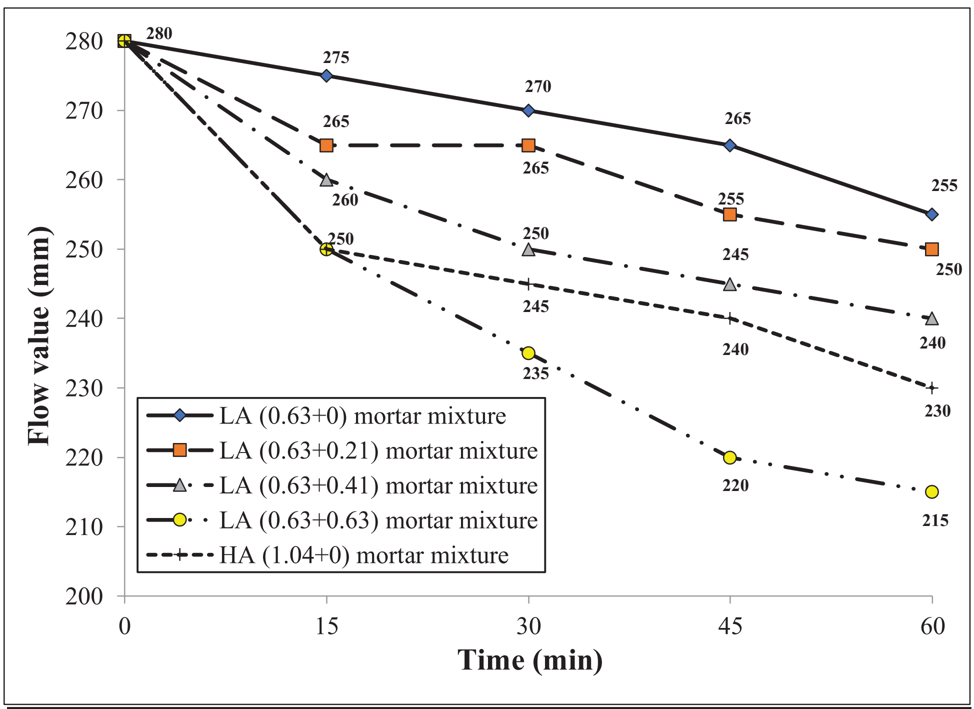


exhibited the worst performance in terms of flowability. As expected, the flow value of all mixtures increased by increasing the HRWR admixture dosage. However, with the increase of the Na_2O_{eq} content, the performance of the water reducing admixture decreased. For example, in the mixtures containing 0.4% HRWR admixture, a 15% reduction in the flow value occurred when Na_2O_{eq} content increased from 0.63% to 1.26%. Besides, the $LA_{(0.63 + 0.41)}$ mortar showed better flowability than the $HA_{(1.04 + 0)}$ mixture, having the same Na_2O_{eq} content.

The time-dependent flow behavior was studied for the mixtures with a fixed flow value of 280 mm (Figure 5). The HRWR admixture requirement for the target flow was found to be 0.25, 0.33, 0.33, and 0.4 wt.% of the cement for $LA_{(0.63 + 0)}$, $LA_{(0.63 + 0.21)}$, $LA_{(0.63 + 0.41)}$, $LA_{(0.63 + 0.63)}$ and $HA_{(1.04 + 0)}$ mixtures, respectively (Figure 4). The relative flow loss at the end of 60 minutes of the mortar mixtures, compared to that of $LA_{(0.63 + 0)}$ mixture, is shown in Figure 6. $LA_{(0.63 + 0.63)}$ mixture showed the highest loss of flow, whereas $LA_{(0.63 + 0)}$ mixture showed the best performance from a flow retention view point.

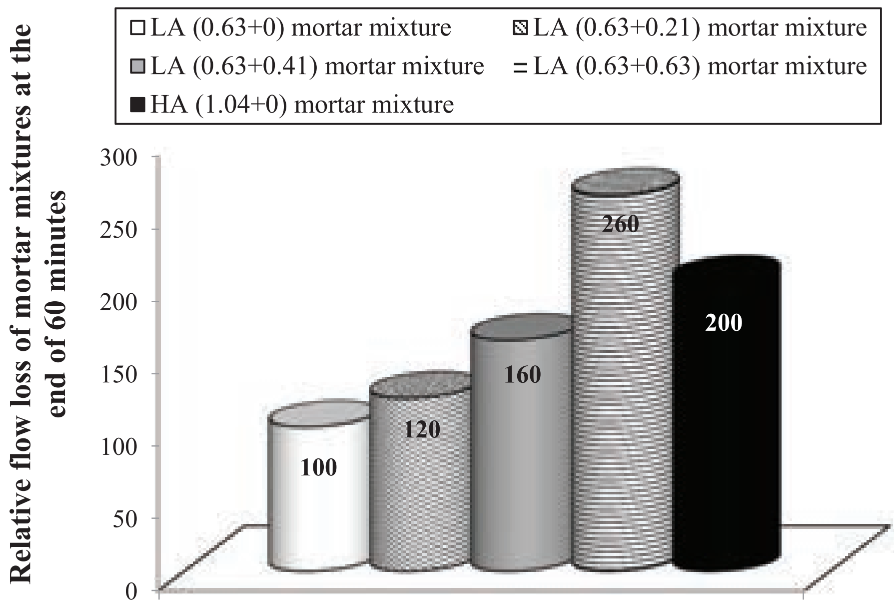
The effect of cement Na_2O_{eq} content on the V-funnel flow time was obtained on mortar mixtures with a flow value of 280 mm. Time-dependent V-funnel flow times of the mixtures were measured at 15-minute time intervals. The mixtures showed no flow after 30 minutes. Therefore, the flow times of the mixtures up to 15 minutes after casting are shown in Figure 7.

FIGURE 5. Flow-time variation and relative flow values of mortar mixtures.



Time (min)		0	15	30	45	60
Relative flow (%)	$LA_{(0.63+0)}$ mortar mixture	100	98	96	95	91
	$LA_{(0.63+0.21)}$ mortar mixture	100	95	95	91	89
	$LA_{(0.63+0.41)}$ mortar mixture	100	93	89	88	86
	$LA_{(0.63+0.63)}$ mortar mixture	100	89	84	79	77
	$HA_{(1.04+0)}$ mortar mixture	100	89	88	86	82

FIGURE 6. Relative flow loss of mortar mixtures et the end of 60 minutes (%).



From the figure, the $LA_{(0.63+0)}$ mixture with the lowest Na_2O_{eq} content was the fastest flowing mixture through the V-funnel. The rate of flow was reduced by increasing the alkali content of cement so that the flow time of the $LA_{(0.63+0.63)}$ mixture, with the highest equivalent alkali ratio, was about 2 times higher than that of the $LA_{(0.63+0)}$ mixture. As in the other experiments, the $LA_{(0.63+0.43)}$ mixture showed a more successful result than the $HA_{(1.04+0)}$ mixture in terms of V-funnel flowability, even though they had the same alkali content.

FIGURE 7. Variation of V-funnel flow time of mortar mixtures by elapsing time.

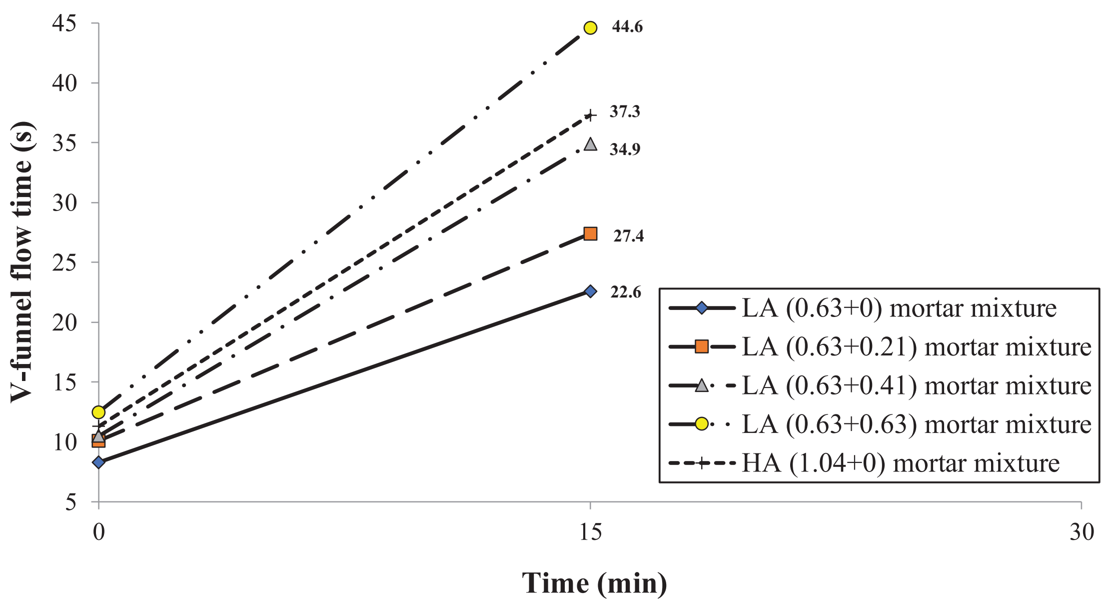
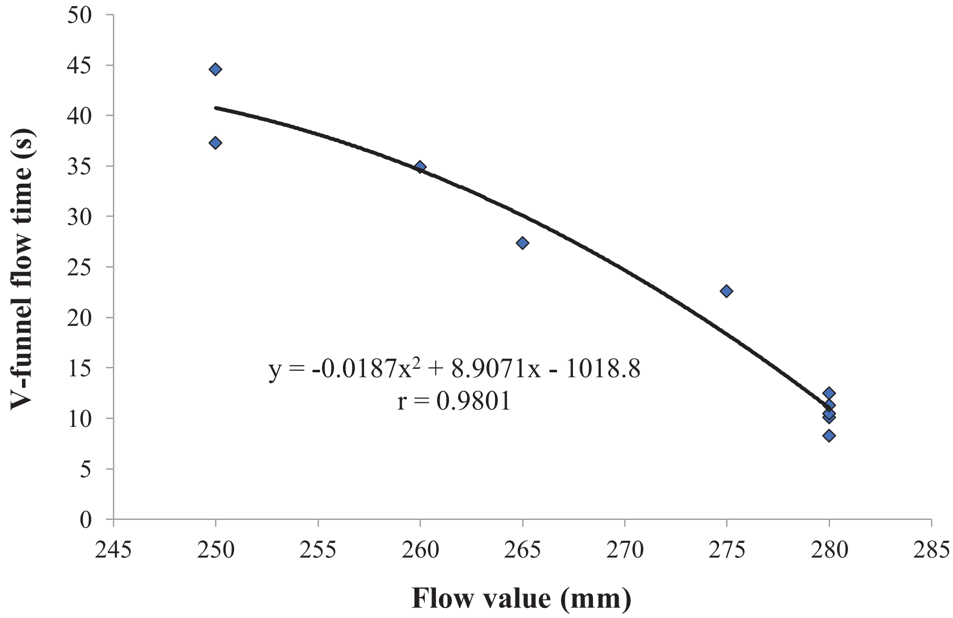


FIGURE 8. Relationship between flow value and V-funnel flow time of mortar mixtures after 15 minutes rest period.



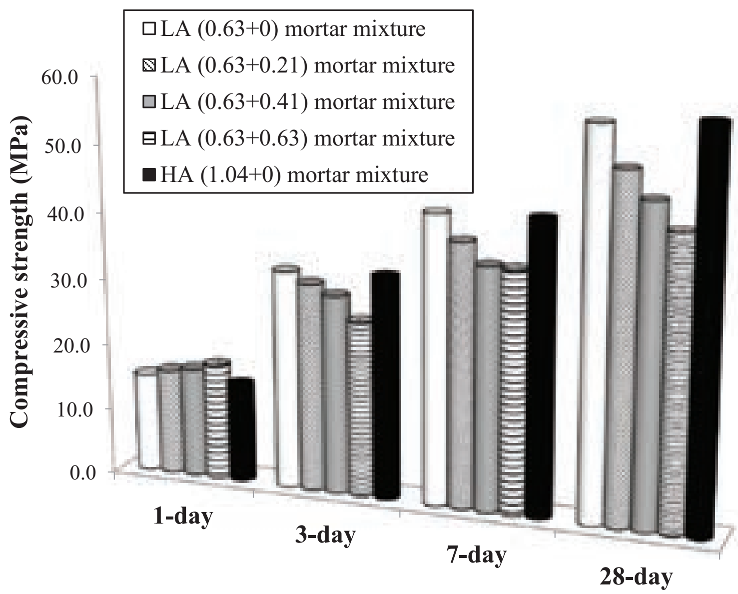
The relationship of flow value and V-funnel flow time after 15 minutes of casting the mortar mixes is shown in Figure 8. As seen from the figure, there is a strong polynomial relationship between the flow and V-funnel flow times of the mortar mixtures.

Test results revealed that the fresh properties of both paste and mortar mixtures were adversely affected by the increase of the Na_2O_{eq} content caused by the NaOH addition. Similar results have been expressed by the other researchers [14, 25]. Claisse et al. [32] reported that detraction of the fresh properties of cementitious systems is caused by increasing the alkali content of cement and resulted from increased C_3A reactivity. Griesser [33] claimed that more ettringite may be formed upon increasing C_3A reactivity in high alkaline medium, resulting in the consumption of a considerable amount of mixing water and lower workability. NaOH solution-free $LA_{(0.63+0)}$ mixture showed better performance than $HA_{(1.04+0)}$ mixture in terms of fresh state properties. This is due to the lower Na_2O_{eq} content and lower fineness of LAcement compared to those of HA cement (Table 1).

The degree of sulfurization, obtained from 100 SO_3/(1.292 Na_2O + 0.85 K_2O) equation proposed by Aitcin, affects the degree of reactivity of C_3A and therefore the type and density of calcium sulfoaluminate hydration products [14]. A high sulfurization degree caused by either high SO_3 content or low alkali content, reduces the reactivity of C_3A which may improve fresh state properties of the mixture.

In this study, sulfurization degree of the HA and LA clinkers were found to be 35.9% and 56.5%, respectively. Accordingly, both cement paste and mortar mixtures produced from the cement having higher clinker sulfurization degree (LA) showed better performance in terms of fresh properties. Similar results were reported by other researchers [34, 35]. Furthermore, it is known that solubility of the alkali added into the mixture is higher than that of the alkali present in the cement components. Therefore, in spite of having same alkali contents, the

FIGURE 9. Compressive strength of mortar mixtures.



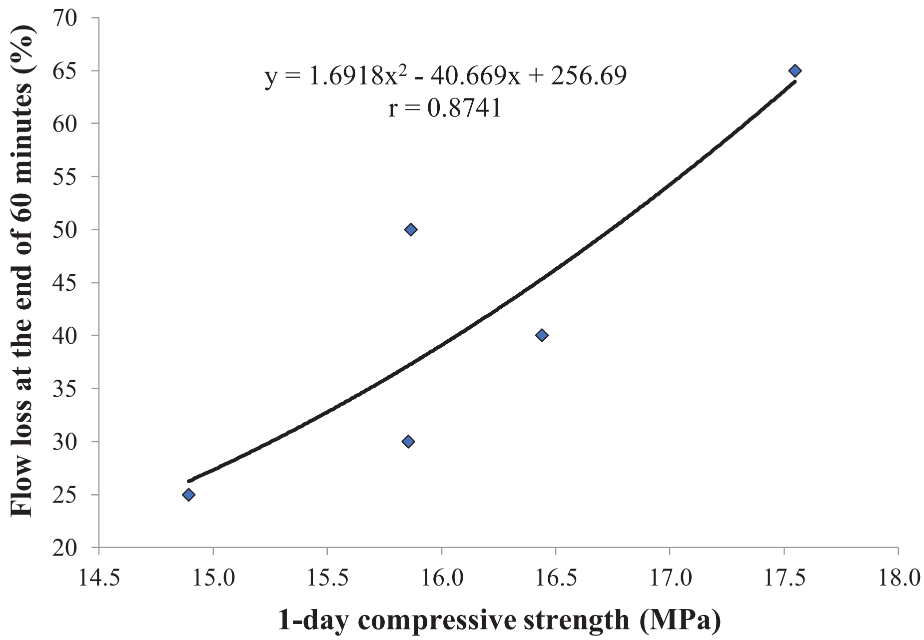
$HA_{(1.04 + 0)}$ mixture was expected to show better fresh properties than $LA_{(0.63 + 0.41)}$. Contrary to this expectation, the $LA_{(0.63 + 0.41)}$ mixture showed better performance than $HA_{(1.04 + 0)}$ in terms of fresh properties. This is thought to result in part from the higher sulfurization degree of LA clinker and in part from the higher fineness of HA cement.

Compressive strength

The compressive strength of mortar mixtures having constant w/c ratio (0.485), sand/cement ratio (2.75) and flow (280 mm), provided by adding various amounts of HRWR admixture (Figure 4), was determined. The results, shown in Figure 9, revealed that among the mixtures, $LA_{(0.63 + 0)}$ having the lowest alkali content, showed the lowest 1-day strength. NaOH inclusion increased 1-day strength of the mix, however, decreased the strength beyond this age. Thus, the $LA_{(0.63 + 0.63)}$ mix showed 25% higher 1-day strength and roughly 30% lower 28-day strength than those of $LA_{(0.63 + 0)}$. This obviously arises from the higher reactivity of C_3A compound (more rapid hydration of cement) which reduces the setting time and meanwhile increases the 1-day strength of the mix [6 and 36]. However, the detrimental effect of nonuniform distribution of hydration products upon rapid hydration results in lower strength at later ages. This result is also evident from the close relationship between 60 minute flow loss and 1-day strength of the mortar mixtures as shown in Figure 10.

As mentioned earlier, Na_2O_{eq} content of $LA_{(0.63 + 0.41)}$ mixture was brought to the same level as that of $HA_{(1.04 + 0)}$ mixture by adding NaOH. Moreover, HA cement has a higher Blaine fineness than LA cement. Besides, it is known that solubility of the NaOH added into the mixture is higher than that of the alkalis present in the cement components. It was observed that the cement fineness and clinker sulfurization degree have a more dominant effect on the short-term (up to 60 min.) fresh properties than the alkali content of the mixture. Thus, $LA_{(0.63 + 0.41)}$ mixture showed better performance in terms of consistency protection than $HA_{(1.04 + 0)}$

FIGURE 10. Relationship between flow loss at the end of 60 minutes from casting and 1-day compressive strength of mortar mixtures.



mixture. The mixture with a shorter setting time was expected to show higher 1-day strength. However, $HA_{(1.04 + 0)}$ mixture showed 10% lower strength than $LA_{(0.63 + 0.41)}$ mixture, despite of its faster loss of consistency. It was understood that the effect of the alkali added into the mixture prevailed during the first 24 hours and was not limited to the first 60 minutes. The higher 1-day compressive strength of $LA_{(0.63 + 0.41)}$ mixture, compared to that of $HA_{(1.04 + 0)}$ mixture, is caused by the higher solubility of alkali added into the mixture. However, this effect was reversed at later ages due to the nonuniform distribution of hydration products upon rapid hydration.

CONCLUSION

For the materials used and tests applied the following conclusions can be drawn:

By increasing the alkali content of the mixtures:

- fresh state properties of the paste and mortar mixtures were adversely affected. Flow time of the cement paste mixtures increased and flow value of the mortar mixtures decreased. This fact was more pronounced when examining the mixes at different time intervals.
- 1-day compressive strength of the mortar mixtures increased, while beyond this age, the strength values were reduced considerably.

Upon addition of 0.63% of NaOH to the mixture, initial and final setting times were reduced by 34% and 44%, respectively, compared to those of the NaOH-free mixture. Besides, 25% more water reducing admixture was found to be required for the saturation point. Moreover, Marsh-funnel flow time of the mixture at the saturation point decreased by 27%. The high alkali content of the cement reduced the effectiveness of the water reducing admixture. Therefore, the amount of cement for a constant w/c ratio can be reduced when low alkaline cement is used. This is an important issue in terms of environmental health.

The high sulfurization degree of the clinker affected the workability of cementitious systems positively. Flow time of the cement paste mixtures decreased and flow value of the mortar mixtures increased

The low alkali cement, having an equivalent alkali content (by NaOH addition), a lower fineness and a longer setting time than those of the high alkali cement, showed a higher 1-day strength than the high alkali cement. Opposite results were measured at later ages.

In spite of having a lower fineness and a longer setting time but a higher clinker sulfurization degree and lower HRWR requirement, low alkali cement showed slightly higher 1-day strength than high alkali cement. At later ages, both of the cements showed equivalent strength values.

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