PROPERTIES OF PORTLAND CEMENT BASED MATERIALS MODIFIED BY SILICA FUME AND MIXED WITH SATURATED LIME-WATER

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ABSTRACT

On the road of minimizing air pollution and global warming by reducing the Portland cement content in Portland cement based mixes, this experimental study was conducted. Maximizing the percentage of Portland cement replaced by silica fume was tried using lime-water instead of water in mixing. That will help availability of CH crystals at early ages for pozzolanic reaction instead of waiting up to C_3S and C_2S hydration products.

The conducted Portland cement based materials included three groups; cement pastes, cement mortars and cement concrete mixes. The main parameters were; type of mixing solution (water or lime-water) as well as the percentages of Portland cement replaced by silica fume. Times of initial and final settings, compressive strength development, existence and intensity of CH crystals with age, pozzolanic activity as well as efficiency of the investigated matrices to delay the corrosion of embedded steel bars were the investigated properties.

Test results show that using lime-water in mixing delays both of initial and final setting times compared with traditional water due to the common ion effect principals. Moreover, combination use of lime-water and silica fume enhances the pozzolanic reaction that was reflected by the strength development at both early and later ages. The existence of CH crystals for higher percentages of silica fume (up to 30%) for further reaction at later ages was observed by XRD results. Moreover, combined use of silica fume and lime-water ensures a high alkaline media around steel bars from the moment of ingredients mixing as long as later ages despite of pozzolanic reaction that was identified from results of chloride attack.

أجرى هذا البحث فى سبيل تقليل تلوث الهواء والاحتباس الحرارى عن طريق تقليل معدلات استهلاك الاسمنت البورتلاندى فى خلطاتة المختلفة. ويهدف هذا البحث الى تعظيم نسب الاسمنت التى يمكن ان تستبدل بالسيليكا فيوم من خلال استخدام ماء الجير المشبع كمحلول للخلط بدلا من ماء الصنبور. حيث ان استخدام ماء الجير يتيح ايونات هيدروكسيد الكالسيوم اللازمة للتفاعل البوزولانى عند الاعمار المبكرة بدلا من انتظار نواتج الهدرجة من C_2S و C_3S.

هذا ولقد شملت الدراسة ثلاثة مجموعات ذات اساس من الاسمنت البورتلاندى العادى وهى العجينة الاسمنتية و المونة الاسمنتية بالاضافة الى خلطات من الخرسانة. كما شملت متغيرات البحث نوع محلول الخلط (ماء الصنبور كمرجعية و ماء الجير) ، بالاضافة الى نسب احلال الاسمنت بالسيليكا فيوم (٠ — ٤٠%) هذا ولقد شملت القياسات زمنى الشك الابتدائى والنهائى وتطور اكتساب المقاومة ومدى تواجد بللورات هيدروكسيد الكالسيوم مع العمر وكفاءة التفاعل البوزولانى بالاضافة الى كفاءة الخلطات الخرسانية المخلوطة بماء الجير فى ممانعة حدوث الصدأ لصلب التسليح بها.

هذا ولقد اظهر تحليل النتائج ان استخدام محلول ماء الجير فى خلط المواد ذات الاساس الاسمنتى أخر حدوث الشك الابتدائى والنهائى بفعل التاثير الايونى مقارنة بالخلطات المرجعية المخلوطة بماء الصنبور. علاوة على ذلك فقد اتضح انه ومع استخدام كل من ماء الجير والسيليكا فيوم معا يعظم من التفاعل البوزولانى والذى اتضح من ارتفاع معدلات اكتساب المقاومة عند الاعمار المبكرة والمتاخرة. بالاضافة الى ذلك فقد تلاحظ وجود بللورات CH عند نسب عالية للسليكا فيوم (٣٠%) وعند الاعمار المتاخرة (٦٠يوم) وذلك من خلال نتائج XRD مما يعنى استمرار التفاعل البوزولانى وعلى النقيض من ذلك فقد تلاحظ اختفاء تلك البللورات للخلطات المخلوطة بماء الصنبور عند ذات الاعمار. هذا ولقد بينت النتائج ان استخدام كل من السيليكا فيوم وماء الجير وفر وسطا عالى القلوية حول اسياخ التسليح منذ بداية خلط المكونات الامر الذى اوضح ممانعة عالية لحدوث الصدا مقارنة بخلطات التحكم مقاسا اما بالمدة المنقضية لحدوث الشرخ الاولى او بنسب الفقد فى الوزن.

Keywords: Lime-water; Portland cement; Pozzolanic materials; Silica fume; Setting time; Hardened properties; Corrosion.

1. INTRODUCTION

Several researchers have studied the use of pozzolanic materials as a mineral addition to cement based composites to obtain construction materials of enhanced engineering properties. That is due to their influence on microstructure and durability of the blended cement composites [1-3].

The sources of the mineral admixtures are the by-products of many industries. The common types of minerals from industrial by-products are fly ash, rice husk ash, silica fume SF or condensed silica fume CSF, blast furnace slag and other slags. The uses of these minerals result in ecological, economic and energy saving considerations [4].

As reported by many authors, supplementary cementing materials such as SF have a beneficial influence on reinforced concrete durability [5]. Laboratory tests of silica-fume concretes have shown a reduction of concrete water permeability and concrete chloride diffusion coefficients [6]. Factors such as fineness, water to cementitious materials ratio, curing temperature and alkalinity of the pore solution have been thoroughly examined in an attempt to explain the reactivity of this material and relate its pozzolanic potential with the evolution of the hydration procedure [7].

A pozzolanic material requires calcium hydroxide $Ca(OH)_2$ or (CH) in order to form strength producing products (pozzolanic activity); whereas a cementations material contains quantities of CaO and can exhibit a self-cementitious (hydraulic) activity. Usually, the CaO content in these materials is not enough to react with all the quantity of the pozzolanic compounds; thus, they also exhibit pozzolanic activity (pozzolanic and cementitious materials). However, these materials are used in combination with Portland cement, which yields on its hydration, the CH essential for their activation [8]. Authors of Ref. [9] reported that SF exhibits higher pozzolanic activity than metakaolin whereas fly ash exhibits lower one compared to that for metakaolin. That is due to chemical and mineralogical compositions, pozzolanic activity, fineness ... etc.

Replacing some of the cement content in concrete mix by mineral admixtures is being recommended aim due to pollution problems. But replacing of cement in concrete by mineral admixtures produces an immediate dilution effect [10]. However an increase in the strength of concrete was observed at later ages. This is due to the well known chemical reaction between pozzolans and CH released from C_3S and C_2S hydration.

In essence, the liberated CH crystals are responsible for the formation of the passive layer around the reinforcement of reinforced concrete members. But when highly active pozzolans materials are used in cement based mixes, they remove CH from the system and accelerate the ordinary Portland cement hydration.

Hydrated lime was used as an admixture in poured concrete in the beginning of the 20th century [11]. That was due to the improved water tightness and impermeability. However, this use has largely disappeared due to increasing strength, finer grinding of Portland cement and the interaction of the chemical admixtures. From other points of view, the employment of pozzolan mixed with lime, of similar fineness to that of the OPC, will reduce the risk of concrete decalcification, even for large substitution volumes, starting by the pH rising of the water contained in pores, which would prevent the reinforcement passive protection [12]. Moreover, the effects of hydrated lime and SF on fly ash concrete in improving its early age strength and other properties were studied [13]. The air permeability of concrete containing lime and SF either decreased or remained almost the same when compared to the concrete without these ones. The addition of lime and SF also improved the sorptivity of concrete.

Due to the trend of using friendly environmental materials in the field of cement and concrete industries, complete utilization of cementitious and pozzolanic by-products are highly recommended [14,15]. However, the need for increased use of supplementary cementing materials in concrete requires more available CH, which was tried through using lime putty addition to concrete mixes. Lime putty addition has been already proved beneficial for durability properties [16].

Authors of Ref. [17] determined compressive strength of SF mortar having proportion 1:1:6 (Cement + silica fume: lime: sand). They concluded that in Portland cement mortars, SF acts mainly at the interface paste-aggregate, where there is a higher concentration of CH and greater porosity than in paste. In Portland cement mortars with SF, lime is better suited in the paste and there is no evidence of concentration of SF at the interface of paste and aggregate.

Through the use of differential scanning calorimetry and thermogravimetric analysis (DSC/TG), it was demonstrated that the addition of hydrated lime increased the $Ca(OH)2$ content; whereas the addition of SF decreased the $Ca(OH)2$ content in the cement paste. The mercury intrusion porosimetry (MIP) data confirmed the beneficial action of hydrated lime and SF, towards decreasing the total pore volume of fly ash cement paste [13].

Since the pozzolanic reaction needs CH crystals to occur and keeping in mind that a period to be waited

until the release of the CH crystals as a product of cement hydration and even after the release of CH crystals they will be consumed by pozzolanic materials through the pozzolanic reaction. All of those draw our attention to the importance of early supply cement based mixes with CH at early ages. This could be achieved by using saturated lime-water LW instead of water W in mixing. Therefore, the objective of the current study is to investigate the influence of using LW in compared with traditional mixing W on setting, hardening and corrosion properties of Portland cement based mixes modified by SF.

2. Experimental Program

An experimental program to evaluate the performance of Portland cement based materials containing SF and mixed with LW instead of W is designed. The efficiency of these modified mixes against chloride attack was conducted. **Tables 1-3** present the schedule of the experimental program.

2.1 Materials

Cement: Ordinary Portland cement with Grade 42.5 MPa was used in this investigation. The used cement is conformed to the Egyptian Standard Specifications (ES) requirements (4756-1/2005).

Hydrated lime: Hydrated lime meets the specifications of ASTM Designation C 207 Standard Specification type N was used as a saturated soluble solution (lime-water LW) instead of tap water W in the proposed mixes. Partial saturated solutions were tried as mixing solutions. The partial saturation percentages were achieved through preparing solutions of LW and traditional W as 0%, 25%, 50% and 100% W to LW solution ratio by volume. LW with pH value of 11 was used for mortar and concrete mixes. On the other hand, saturated lime solution as a mix with W with different replacement percentages as 0%, 25%, 50%, 100% by volume of W were used for cement paste mixes. The prepared mixtures had pH values as 8, 9, 10 and 11, respectively. The corresponding measured total dissolved salts TDS values were 1000, 1000, 1100 and 1900 ppm for the mixtures in the same order, respectively. Details of these parameters are shown in **Table 1**.

Aggregates: Medium well-graded sand of fineness modulus 2.27 was used. Natural well-graded gravel of 20 mm maximum nominal size was used; it included a combination of round and angular particles. The fine and coarse aggregates conformed to the ES requirements (1109-2002). The grading curves for the used aggregates are given in **Fig. 1**.

Silica fume: SF of mineral admixtures was used as replacement of cement by mass. It had 150,000 cm^2/gm specific surface areas as given by the manufacturer.

2.2 Specimen fabrication and component tests

In general, LW is made using hydrated lime by the addition of W to make a saturated solution. In terms of solids (lime) content, this works out to be a mixture that is approximately 15% to 20% lime and 80% to 85% water after this procedure the soluble was left for enough time to deposit, and then the clear water of saturated lime was used.
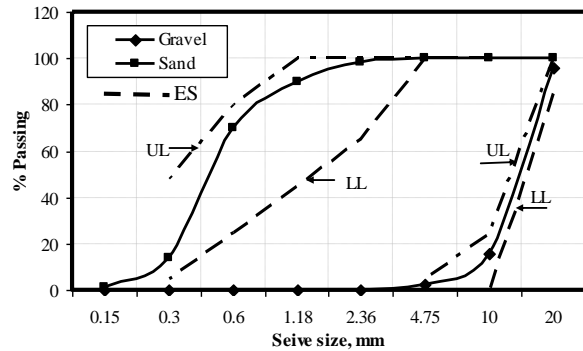

Fig.1: Grading of the used aggregates

2.2.1 Cement paste mixes

Twelve cement paste mixes were designed to study the effect of LW on cement hydration and the interaction with the SF. Cement pastes of standard consistency were prepared according to ASTM C 187 – 98 [18] by using Vicat apparatus. SF with 0%, 10%, 20%, 30% and 40% replacement by cement mass were investigated by using ordinary W and LW, **Table 1** presents the cement pastes under investigation and the results of Vicat test. The specimens in their moulds (Vicat moulds) were covered with a plastic sheet and kept in the casting room at 20(±1) °C for 24 hr. These were then demoulded and covered with a plastic sheet, where they remained until required age for XRD testing. XRD patterns of the hydrated samples were recorded at 3, 7, 28 and 60 days using a GNR APD 2000 PRO model X-ray diffractometer (CuKa α radiation, 40 kV, 30 mA) in a scanning range of 5–65° in 2θ scale. The testing rate that was applied was 0.02°/s for all test specimens.

Table 1: Schedule of program for cement paste mixes and results of Vicat test

Code of cement paste mix	Type of mix solution	SF, %	W/(C+SF)	TDS, PPm	Setting time, min	
					Initial	Final
P0W (Control)	W	-	0.3	1000	105	215
P025LW	(25+75) (LW+W)	-	0.3	1000	105	220
P050LW	(50+50) (LW+W)	-	0.3	1100	115	235
P10W	W	10	0.33	1000	160	220
P20W		20	0.38	1000	165	265
P30W		30	0.45	1000	150	275
P40W		40	0.54	1000	135	300
P0LW (Control)	LW	0	0.3	1900	135	245
P10LW		10	0.33	1900	170	250
P20LW		20	0.38	1900	195	288
P30LW		30	0.45	1900	165	295
P40LW		40	0.54	1900	150	330

2.2.2 Cement mortar mixes

Eight mortar mixes were cast and tested. Mortar cubes measuring 70 x 70 x 70 mm were made to record the compressive strength of mortar up to 60 days. SF with 0%, 10%, 20% and 30% replacement by cement mass were conducted (refer to **Table 2**). A universal testing machine of 300 kN total capacity was used. An electrical driven mechanical mixer of 3 L total capacity was used. The mixing procedure includes pre-mixing the SF (when present) with the cement, adding the mixing W or LW when applied until wet, and then adding the aggregate in preparation for final blending. Final mixing proceeded for 3 min, was halted for one minute, while the mixing bowl walls were scraped down, and resumed for a second period of 2 min. The mixes were cast in steel cubes molds and were vibrated for 10 sec on a vibrating table to aid in consolidation. All cubes were demolded after 24 hrs with some being set aside to comprise the 1-day samples. The remainder were placed in water and cured until the age of testing.

Table 2: Schedule of program for mortar mixes

Code of mortar mix	Type of mix solution	SF, %	Mix Proportion by weight	Tests
M0W (control)	W	0	1: 2.5: 0.5 C+SF: S: W	-Compressive strength at (3,7 ,28 and 60) days
M10W		10		
M20W		20		
M30W		30		
M0LW (control)	LW	0	1: 2.5: 0.5 C+SF: S: LW	
M10LW		10		
M20LW		20		
M30LW		30		

2.2.3 Concrete mixes

Eight concrete mixes were cast and tested. SF with 0%, 10%, 20% and 30% replacement by cement mass were investigated. Concrete cubes measuring 150 x 150 x 150 mm were prepared to follow the compressive strength gain of concrete up to 60 days (refer to **Table 3**), a hydraulic testing machine of 1550 kN total capacity was used. The concrete mixes were mixed as the same sequences established for mortar mixes using mechanical mixer of 100 L capacity. After complete mixing, slump test according to the procedure described in Egyptian Code ECP 203:2009 and ASTM C143 standards, was conducted to keep plastic consistency for all mixes. All specimens were cured by immerging in a water tank at 20 ^{0}C until the day of testing and for a total curing period of 28 days. After 28 days, the specimens were left in laboratory conditions. Moreover, the influence of these modified concrete mixes on steel corrosion resistance was investigated using concrete cubes specimens of 150 mm side dimension. The specimens were prepared and steel bar of 10 mm in diameter were placed in the center of the concrete cube to 100 mm depth. The specimens were exposed to 5% NaCl solutions at a depth of 50 mm in fiberglass container after 28 days from casting and curing. An accelerated test for corrosion was applied by using power supply at constant current and switch to suitable voltage. Stainless steel bar with 10 mm diameter was used as a cathode and the steel bar act as an anode up to the cutting of the electrical cell due to the cutting the steel bars and /or over all 120 days.

Figure 2 shows the accelerated corrosion cell arrangement. After then the specimens were taken out from the container and the steel reinforcement was extracted from the specimens and then cleaned carefully to remove the rust from the steel bars. Then the steel reinforcement bars were weighted and the percents of weight loss were calculated.

Table 3: Schedule of program for concrete mixes

| Code of concrete mix	Type of mix solution	SF, %	Mix proportion by mass	Tests	
				Fresh	Hardened
C0W (control)	W	0	400:0:675:1015:200 C:SF:S:G:W	- Slump - Setting times	-Compressive strength at (3, 7, 28 and 60) days - Exposure to NaCl at 28 days
C10W		10	360:40:675:1015:200 C:SF:S:G:W		
C20W		20	320:80:675:1015:237 C:SF:S:G:W		
C30W		30	280:120:675:1015:250 C:SF:S:G:W		
C0LW (control)	LW	0	400:0:675:1015:200 C:SF:S:G: Lw		
C10LW		10	360:40:675:1015:200 C:SF:S:G: Lw		
C20LW		20	320:80:675:1015:237 C:SF:S:G: Lw		
C30LW		30	280:120:675:1015:250 C:SF:S:G: Lw		
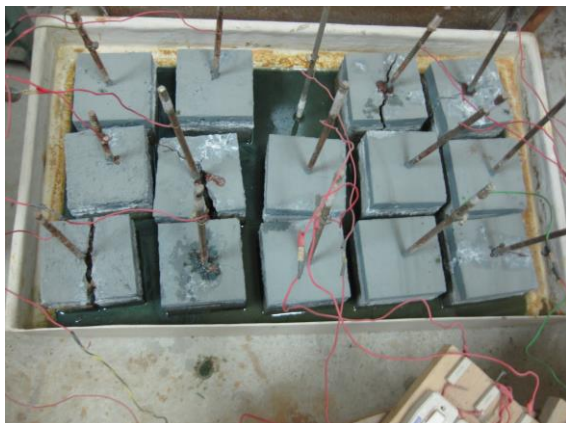
Fig.2: The accelerated corrosion cell arrangement

3. Results and discussion

Replacing part of cement in Portland cement concrete mixes is a target in the road of minimizing air pollution and global warming. The following Sections present the properties of Portland cement based materials mixed with either W or LW solution. Setting properties, hydration process as well as corrosion rate of embedded steel bars are the main properties evaluated in this study.

3.1 Initial and final setting times
3.1.1 Cement paste mixes

To investigate using of LW solution as a mixing solution, a preliminary study aimed at evaluating the degree of saturation on setting properties was conducted. The results of this study are given in **Table 1.** The tried degrees of saturations were 0%, 25%, 50% and 100%. The recorded initial times of setting were 105, 105, 115 and 135 min for the conducted mixes, respectively. Whereas, the final setting times for the same mixes were 215, 220, 235 and 245 min, respectively. These results concluded that the best retardation was achieved with using LW at 100% degree of saturation.

The results of both initial and final setting times are presented in **Fig. 3**. Two series were conducted; first one was conducted using W as a mixing solution whereas, second one was conducted using LW as a mixing solution. For both series, SF was used as a partial replacement of cement by weight. The conducted replacement ratios were 0%, 10%, 20% 30% and 40%.

For mixes made up of W and containing SF, it can be noticed from **Fig. 3** that with increasing SF content, a delay in initial setting times were observed compared to the control mix P0W. The initial setting time values are 105, 160, 165, 150 and 135 min for mixes P0W, P10W, P20W, P30W and P40W, respectively. The maximum retardation of initial setting time was recorded for mix P20W with 57.14% over the control mix P0W. Moreover, the final setting time values were 215, 220, 265, 275 and 300 min for mixes P0W, P10W, P20W, P30W and P40W, respectively. The maximum increase in the retardation was recorded at 40% replacement as 39.5% over the control mix P0W.

The noticed retardation in both initial and final setting times for mixes containing SF and mixed with W agree well with many previous studies [19, 20].

On the other hand and with using LW as a solution in mixing, a shift in both initial and final setting times indicating retardation in both times was noticed compared with using W, as given in **Fig.3**.

That retardation could be explained as the hydration of C_3A is retarded by CH ions, which react with C_3A and water to form C_2AH8 and C_4AH_{19} that form a protective layer or coating on the surface of un-hydrated grains of C_3A. Upon conversions of these initially formed hydrates to cubic C_3AH_6, the barrier is disrupted and the hydration proceeds again with a fairly high speed [21].

The values of initial setting times for cement pastes made up of LW and SF were recorded as 135, 170, 195, 165 and 150 min for mixes P0WL, P10LW, P20LW, P30LW and P40LW, respectively. Whereas, the final setting times were recorded as 245, 250, 288, 295 and 330 min for the same mixes, respectively. The maximum delay in initial setting time was recorded for mix P20LW as 44.4% over the control mix P0LW whereas, the beigest delay in final setting time was recorded for mix P40LW as 34.7% over the control mix P0LW. These delayed values are 85.7% and 53.5% over that for control mix P0W.

Using both of SF and LW in a cement paste mix tends to delay both of initial and final setting times. The retardation part due to SF agree well with results of reference [22], which could be related to the higher specific surface area for SF that requires an increase of water demand to achieve the standard consistency.
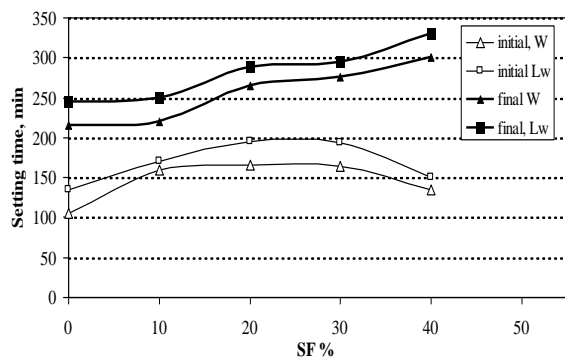

Fig. 3: Initial and final setting times for cement pastes

3.1.2 Concrete mixes

The results of the initial and final setting times for different concrete mixes are presented in **Fig.4**.

Mixes mixed using LW seem to be delayed in initial setting times. Moreover, the delay exceeds with higher SF content, the values of initial setting times were recorded as 200, 240, 270 and 327 min for mixes C0W, C10W, C20W and C30W, respectively. Whereas, the corresponding values for mixes C0LW, C10LW, C20LW and C30LW were 254, 291, 333 and 366 min, respectively. The maximum delayed values were recorded at 30% SF for both mixes made up of W and LW. The curve representing initial setting times for mixes made up of LW seem to be parallel to that for mixes prepared with water. This shift could be considered as the influence of using LW in causing the retardation. The maximum delay periods were noticed at 30% SF as 63.5% for mix C30W over the control mix C0W. Whereas, the maximum delay in initial setting time was recorded at 30% SF mixed with LW was 44.1% over mix C0LW.

The difference in retardation period between mix C30LW and C0W gives the combined effect of both of SF and LW in the retardation of the initial setting time that achieves 83% over that of the control mix C0W.

The trend previously noticed with initial setting times was noticed for final setting times as well. Moreover, the maximum delay in final setting time for mixes containing SF was noticed at 30% SF and mixed with W which approaches 57% over the control mix C0W. The highest delay of final setting times for mixes mixed with LW was noticed at 30% SF that approaches 43% over the corresponding control mix C0LW. The combination influence of both SF and LW gives the highest value for delay in final setting times that is the difference between final setting times for C30LW and C0W. The delay of final setting time approaches the maximum value at C0LW compared to C0W. The recorded delay was 86% over control mix C0W.
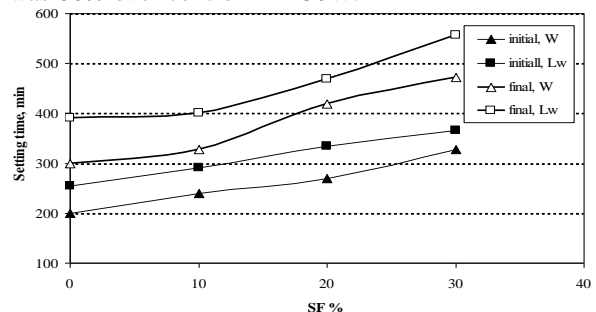

Fig. 4: Initial and final setting times for concrete mixes

3.2 Compressive strength development
3.2.1 Strength development for mortar mixes
Two groups of Portland cement mortar mixes were conducted. First group was mixed with W and contained different percentages of SF as partial replacement of cement weight. The compressive strength was investigated at 3, 7, 28 and 60 days. The results are presented in **Table 4** and **Fig. 5**. It could be noticed that the compressive strength for mortar mixes increases with the increase of SF replacement with cement by weight up to a certain SF content beyond which the strength was decreased. The maximum enhancement in compressive strength was achieved at 20% SF for mix M20W as 15% over the control mix M0W at 60 days age. Whereas, for second group that was mixed with LW, at early ages, the compressive strength values seem to be higher compared to those for corresponding mortar mixes made up of W at similar ages. Moreover, and with increasing the SF content, the measured compressive strength was increased up to the maximum investigated SF content 30%, the same trend was noticed at all the investigated ages 3, 7, 28 and 60 days. The maximum enhancement was recorded at 30% SF for mix M30LW as 52% over the control mix M0W as shown in **Fig. 5**. In contrary and for the mix without SF M0LW a reduction of the compressive strength was noticed at all ages.

Table 4: Test results of mortar mixes compressive strength at different ages

Mix Code	Type of mix solution	SF, %	Compressive strength, MPa			
			3	7	28	60
M0W (control)	W	0	4.1	5.8	7.7	8.9
M10W		10	3.6	5.0	8.8	9.9
M20W		20	3.4	5.0	8.2	10.2
M30W		30	3.3	5.2	8.1	10.1
M0LW (control)	LW	0	3.8	5.4	7.5	8.3
M10LW		10	4.0	6.0	9.2	10.7
M20LW		20	4.3	7.3	10.5	12.4
M30LW		30	4.4	7.2	11.5	13.5

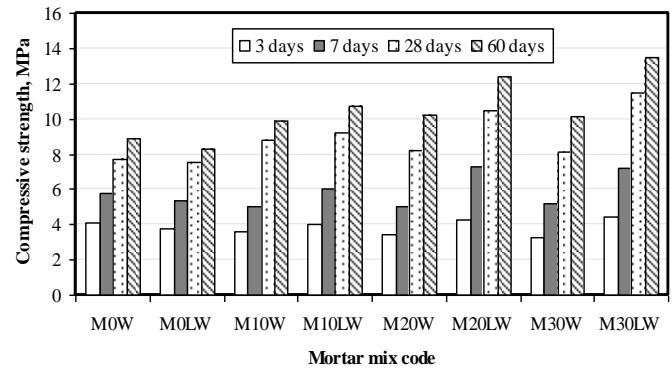**Fig. 5**: Compressive strength for mortar mixes at different ages

3.2.2 Strength development for concrete mixes
Two groups of concrete mixes were investigated for compressive strength development. The first one was a series of Portland cement concrete mixes mixed with W and contained 0, 10, 20 and 30% SF and indexed as C0W, C10W, C20W and C30W, respectively. Moreover, the second group was mixed with LW and contained 0, 10, 20 and 30% SF and indexed as C0LW, C10LW, C20LW and C30LW, respectively. The compressive strength results for both groups are presented in **Table 5** and **Fig. 6**.

For first group, it can be noticed that the compressive strength increases with the increase of SF content up to a certain content beyond which the strength is decreased. **Figure 6** shows that at 20% SF, higher strengths have been achieved at 28 and 60 days age. The maximum enhancement at 60 days age is 12% for C20W over the control mix C0W.

For second group for which LW is used, it can be noticed that the measured compressive strength values increase with the increase of SF content up to the maximum used SF content 30%. Remarkable enhancements are recorded at both early ages and late ages as well. For mix C30LW the enhancements are 21%, 30%, 20% and 32.2% over the control mix C0W at 3, 7, 28 and 60 days age, respectively.

For mix without SF and mixed with LW (mix C0LW) reduction of the measured compressive strength values are noticed at all ages compared to mix C0W and 10.7% decrease of the compressive strength is recorded at 60 days age. This reduction may be due to the retardation phenomena previously noticed with setting times.

Table 5: Test results of concrete mixes compressive strength at different ages

Mix Code	Type of mix solution	SF, %	Compressive strength, MPa			
			3	7	28	60
C0W (control)	W	0	10.5	18.0	26.0	28.0
C10W		10	10.0	19.0	23.4	25.0
C20W		20	8.5	17.5	29.0	31.4
C30W		30	8.1	15.5	27.5	30.8
C0LW (control)	LW	0	9.0	15.2	23.4	25.0
C10LW		10	11.0	20.0	30.0	33.4
C20LW		20	12.0	22.0	29.5	35.0
C30LW		30	12.7	23.4	31.2	37.3

3.3 Consumptions of CH crystals

To follow up the pozzolanic reaction of SF with and without LW, XRD analysis was conducted at different ages and the pattern are shown in **Figs. 7-11**. The consumptions of CH crystal contents could be demonstrated approximately by intensity changes of main diffraction peaks of CH crystals, such as B1 crystal face, as well as B2 and B3 crystal faces (d=0.490, 0.310 and 0.263 nm, respectively [20], where d; lattice spacing in a crystalline sample as given by the well known Bragg's law). At the same ages, diffraction peak intensities of B2 and B3 crystal faces of CH for the investigated samples were almost close to those for control samples. In contrary, noticeable differences were recorded at the intensities of B1crystal face.

Considering the intensities of B1 it could be noticed that the intensity values for all mixes mixed with LW are higher compared to the corresponding mixes mixed with W. The trend was noticed for mixes without SF as well as those containing 10%, 20% and 30% SF at different ages as given in **Figs. 7-11**.

Due to the high content of CH crystals contained in mixes made up of LW this can help maximizing the replacement of cement by SF. **Figure 11** shows the XRD patterns for all mixes containing 30% SF at different ages. Moreover, it could be realize that at early ages, the intensity of CH crystals are higher for mixes made up of LW compared to those mixed with W, whereas, at 60 days age, the CH crystals are consumed in mix containing 30% SF and there was still an amount of CH crystals in mix C30LW available for further pozzolanic reaction to take place to form more of Calcium Silicate Hydrate CSH. That result supports the enhancement in compressive strength especially at later ages for mortar and concrete mixes at higher percentages of SF 30% compared to 20% for mixes made up of W. Moreover, and science the CSH phase is nearly amorphous material, its structure cannot be studied by XRD [21]. The measured compressive strengths could be considered as a measure for the formation of CSH resulting from both of hydration process of cement as well as the pozzolanic reaction.
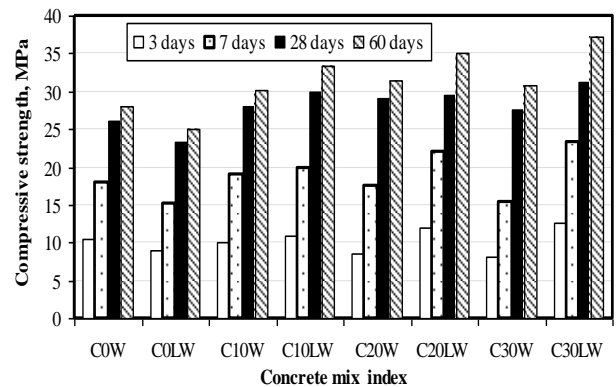

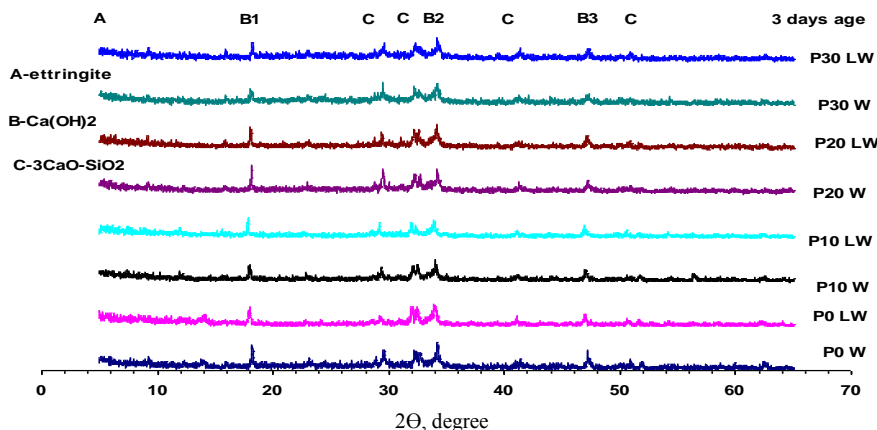**Fig. 6**: Compressive strength for concrete mixes at different ages

Fig. 7: XRD patterns for cement pastes containing SF at 3 days age
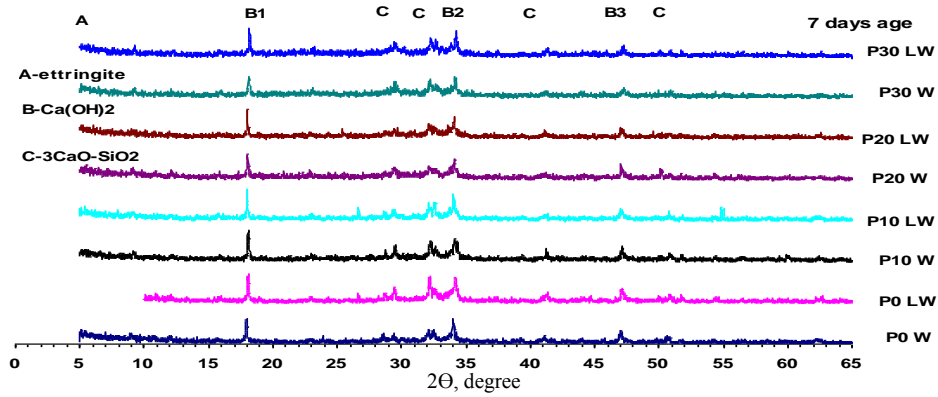
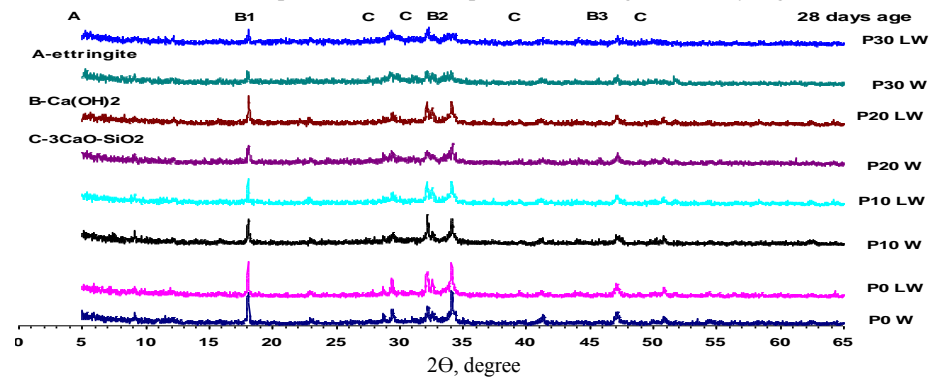**Fig. 8:** XRD patterns for cement pastes containing SF at 7 days age

Fig. 9: XRD patterns for cement pastes containing SF at 28 days age
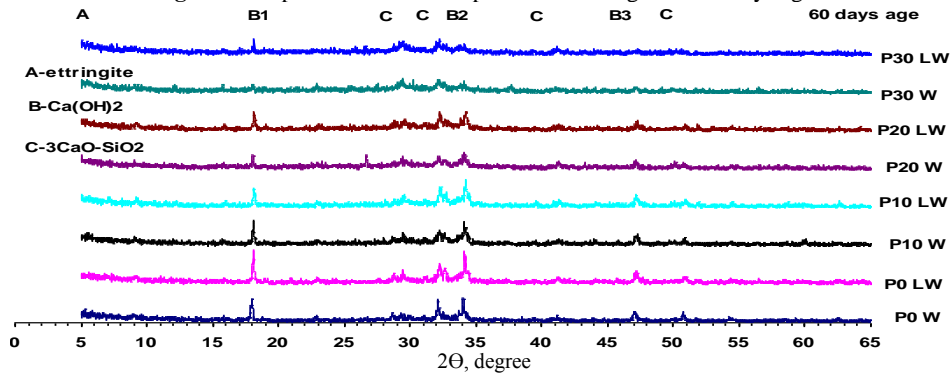

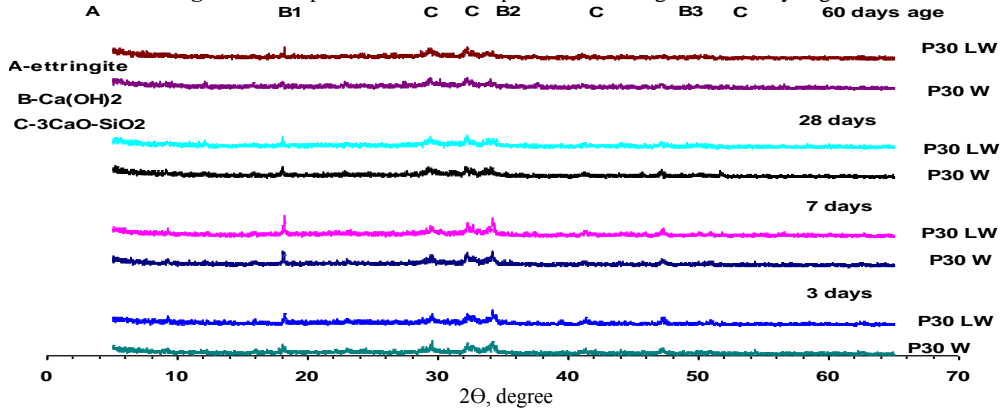**Fig. 10:** XRD patterns for cement pastes containing SF at 60 days age

Fig. 11: XRD patterns for cement pastes containing 30% SF at different ages

3.4 Corrosion resistance of modified concrete mixes

Using LW as a concrete mixing solution parallel with SF was evaluated on corrosion characteristics. An accelerated corrosion test procedure was adopted as presented in **Fig. 2**. Periods to first crack as well as the mass loss measurements were the evaluated parameters. **Figure 12** shows the interface between the extracted steel bars and concrete after exposure for mixes C0W and C30LW, respectively. Whereas, the final appearance of the extracted steel bars at the end of the exposure test to chloride are presented in **Fig. 13**.

Periods to first crack are presented in **Fig. 14**. The periods to fist crack are 50, 90, 92 and 194 days for mixes C0W, C10W, C20W and C30W, respectively. Whereas, for mixes mixed with LW the corresponding elapsed period are 54, 120, 140 and 260 days for C0LW, C10LW, C20LW and C30LW, respectively. It could be noticed that using LW alone in mixing dose not significantly influences the elapsed time to first crack. Moreover, replacing part of Portland cement with SF extended the period required for first crack for mixes mixed with water which my be related to the relatively dense microstructure of mixes containing SF. Furthermore, better results of delaying the occurrence of the first crack was achieved when both of SF parallel with LW was used in concrete mixes. That retardation may be due to the denser structure, which is created when LW and SF are added to concrete mixes as well as the formed passive layer surrounding steel bars.

Losses of embedded steel bars as an indicator for corrosion resistance are presented in **Fig. 15**. Percentages of mass loss for mixes mixed with W are 29, 19, 12 and 17% for mixes C0W, C10W, C20W and C30W, respectively. Whereas, for mixes mixed with LW the corresponding loss percentages are 27, 15, 11 and 4% for mixes C0LW, C10LW, C20LW and C30LW, respectively. Remarkable enhancements in corrosion resistance are clear especially when LW parallel with SF are used, **Figs. 12-15**. With increasing SF in concrete mix and with the existence of LW the microstructure becomes denser and the permeability is decreased which consequently leads to better resistance to corrosion.

The positive results of using SF on retardation and making a resistance to corrosion could be agreed well with the results reached in reference [23].
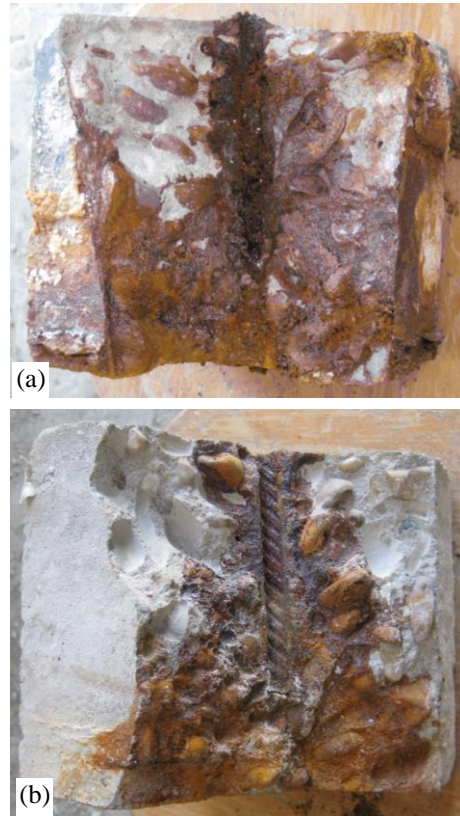
(a)

(b)

Fig. 12: Interface between the corroded steel bars and concrete (a; C0W and b; C30LW)

Fig. 13: Corroded steel bars due to chloride attach at the end of the test (1; COW. 2; COLW, 3;C10W, 4; C10LW, 5; C20W, 6; C20LW, 7; C30W, 8; C30LW)
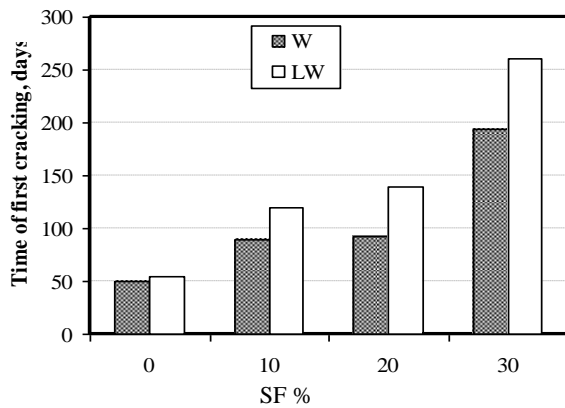
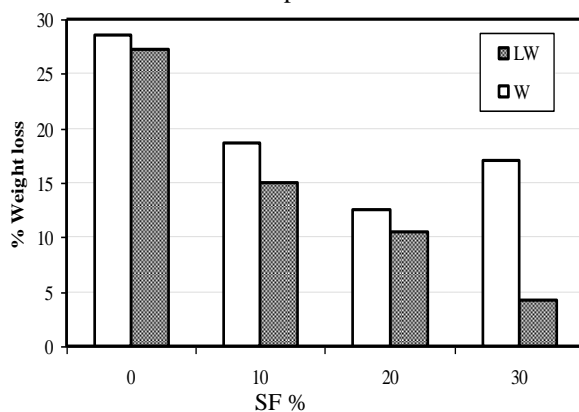**Fig. 14**: Time to first crack for the attached concrete specimens

Fig. 15: Percentage of weight loss of the corroded steel bars due to the chloride attack

4. CONCLUSIONS

Combination use of SF and LW in mixing Portland cement based composites affects both of fresh and hardened properties as well as performance of concrete mixes. Based on the test results and discussion, the following conclusion could be drawn for the current study as follows:

1. Using of LW as a mixing solution delays both of initial and final setting times for Portland cement based materials as well as mixes containing SF. The maximum delay was recorded for cement paste as 90 min and 115 min for initial and final setting times for mixes P20LW and P40LW over the control mix P0W, respectively.
2. The combined use of SF and LW in Portland cement concrete mixes delayed both of initial and final setting times. The maximum delay in initial setting time was noticed for mix C30LW as 83% over the control mix C0W. Moreover, 86% delay of final setting times was recorded for mix C30LW over the control mix C0W.

3. Using LW as a mixing solution delays the strength development at both early and late ages. Whereas, combination use of LW and silica fume enhances both of early and late strengths for cement mortar and concrete mixes.
4. 12% maximum increase of compressive strength for mix C20W was achieved at 60 days age. Whereas, 32% increase of the compressive strength was reached for mix C30LW at 60 days age over the control mix which means 30% SF replacement of cement weight could be achieved and give better enhancement in compressive strength when replacing tap water by LW in mixing.
5. Based on XRD results, Portland cement based mixes mixed with LW can consume large amount of SF compared with those mixed with water. For best compressive strength, mixes made up of water can consume10-20% SF as a replacement of cement whereas, LW mixes can consume 30% or more as a replacement of cement by mass.
6. From durability point of view, when LW is used in concrete mixing which contains SF, significant delays in first crack as well as a decrease in the mass loss of steel bars are observed. For such mixes, an extension of the service life time periods are expected.

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