ISRAA UNIVERSITY JOURNAL OF APPLIED SCIENCES
ISSN: 2523-0522
Volume3: Issue1, October, 2019

The Activity of HYPR surfactant as Superplasticizer on the properties of concrete mixes

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ABSTRACT

Superplasticizers are a basic component in a today concretes, enhancing workability, which leads to producing durable and sustainable concrete. This research aims to study the effect of Alkyl dimethyl hydroxyl ethyl ammonium chloride (HYPR) cationic surfactant as superplasticizer on the properties of concrete to produce concrete with suitable workability. The mechanical properties concrete mixes first obtained for control mix, then for different concentration of HYPR that added to the concrete, 0.10, 0.25, 0.50 and 0.75% by cement weight. The slump tests, air content, compressive strength tests , microstructure and morphology of the hardened concrete were conducted for all specimens with and without HYPR. The results indicate that using HYPR admixture at their best ratios in the concrete mixes would improve the slump loss from 70 mm to 230 mm. The use of HYPR admixture showed an adverse effect on compressive strength. The scanning electron microscope (SEM) illustrates that the addition of HYPR on concrete produces consistent bubble structure with a uniform small air voids system (80.41 µm).

Keywords: Superplasticizer, compressive strength, air content, HYPR, surfactant, slump.

ISRAA UNIVERSITY JOURNAL OF APPLIED SCIENCES ISSN : 2523-0522
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1. Introduction

Superplasticizers are chemical admixtures providing workability enhancement at low water to cement ratios (W/C) which leads to producing durable and sustainable concrete.

The main action of the superplasticizers is to wrap themselves around the cement particles and give them a highly negative charge so that they repel each other, by repelling action cement particles are deflocculated and dispersed releasing water confined inside them.

The workability can be enhanced by using the exact required amount of superplasticizer (Andersen, 1986) and (MacInnis and Racic, 1986). Usually, manufacturers indicate the effects of such admixture; however, their action and performance should be checked before use (Baalbaki, and Aitcin, 1994). When concrete is fresh, it is desirable to be malleable or workable. However, sometimes, due to scorching conditions at the site, desirable workability cannot be maintained. Then superplasticizer enhances the workability to a sufficient extent by lowering the shear and flow resistance [Golaszewski, and Szwabowski, 2004]. Even in the case of self-consolidating concrete, superplasticizer greatly enhances the workability of concrete (Felekoglu, and Sarıkahya, 2008) and (Sahmaran, et. al 2006). Normally, the chemical admixtures used for reducing water are liquids and have less than 0.5 percent of cement weight. In these chemical admixtures, solid's contribution ranges from 30 - 40% of total volume. In low range water reducing admixtures, high retardation and bleeding may take place but, comparatively, high range water reducing admixtures can be added from 0.7- 2.5% of cement weight [Hameed, 2012].

HYPR belong to a chemical family called surfactants, surfactants are amphipathic molecules, which have two characteristics, polar head, and non-polar tail, in different parts of the same molecule. Therefore, a surfactant molecule has both hydrophilic and hydrophobic characteristics. Surfactants are classified, based on the charged groups present in their heads, into the following four categories: [Qaraman, 2017) Anionic, cationic, non-ionic and amphoteric or zwitterionic. HYPR is a cationic surfactant, which has an appositive charge in its head.

The main aim of research is to study the effect of (HYPR) as superplasticizer on the fresh and hardened properties of concrete to produce concrete with adequate workability.

2. Experimental

2.1 Materials

2.1.a Surfactant

Different cooncentration 0.10, 0.25, 0.50 and 0.75% are used of the surfactant Alkyl dimethyl hydroxyl ethyl ammonium chloride (HYPR) which supplied from Clariant, the HYPR surfactant structure is:

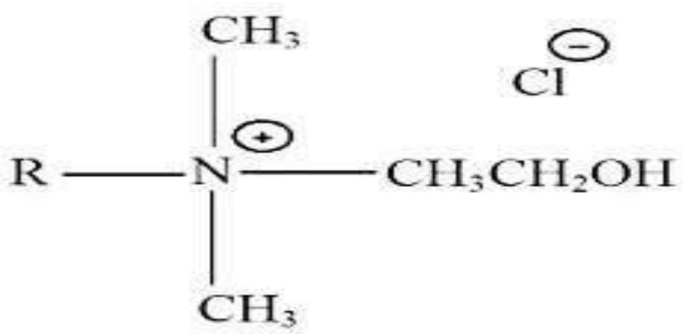

Figure 1: Alkyl dimethyl hydroxyl ethyl ammonium chloride (HYPR) chemical structure

2.1.b Cement

The cement used is Portland cement of mark CEM I 52.5N obtained from El-Arish cement factory. Its chemical composition is given in Table (1).

Table (1): Chemical composition of the used ordinary Portland cement (OPC). (Qaraman et al ,2016)

Oxide (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	Cl^-	MgO	SO_3	Free CaO	Ignition Loss
OPC	22.12	5.56	3.69	62.87	0.29	0.11	0.02	2.36	0.91	0.92	1.22

The cement tested according to ASTM C109, C187, C191 and C204 and the result are accepted according to the specification of ASTM C150. The results physical and a mechanical properties and the specification requirement according to ASTM C150 of the cement was mentioned in Table (2).

Table (2): Cement characteristic according to testing and (ASTM C150)

Type of test	Related ASTM specification	Characteristic	Result	Cement Type I ASTM C150
Setting time using Vicat test (minutes)	C191	Initial	105	>60
		Final	315	<600
Mortar compressive strength (MPa)	C109	At age 3 days	13.5	Min 12
		At age 7 days	29.6	Min 17
		At age 28 days	47.3	No limit
Blain fineness (cm^2/g)	C204	-	3035	Min. 2800
Water demand (%)	C187	-	27.5	No limit

2.1.c Aggregate

The coarse and fine aggregate physical properties are listed as below:

2.1.c.1 Sieve analysis

The coarse and fine aggregate sieve analysis was done according to ASTM C136; the result was listed in the Table (3).

Table (3): results of coarse and fine aggregate sieve analysis

Sieve #	Sieve Size	Sample Name Type I (FOLIIA)	Type II (ADASIA)	Type III (SMSMIA)	Type IV (Sand)
1.5"	**37.5**	100.00			
1"	**25**	98.56			
3/4"	**19**	59.80	100.00		
1/2"	**12.5**	1.78	55.44	100.00	
3/8"	**9.5**	0.00	8.95	95.20	

#4	**4.75**	0.00	0.00	23.32	
#8	**2.36**	0.00	0.00	0.20	100.00
#16	**1.19**				94.45
#30	0.6				76.77
#100	**0.18**				1.05
#200	**0.075**				0.00

3. Specific Gravity and Absorption

The specific gravity and absorption of coarse and fine aggregate was done according to ASTM C 127 and ASTM C 128 and the results are listed in Table (4).

Table (4): . Specific Gravity and Absorption of coarse and fine aggregate

Sample Name	Absorption After 24 hour	Specification	Apparent specific gravity	Bulk specific gravity	Bulk specific gravity in SSD
Type I	1.25%	Max. 2%	2.654	2.549	2.588
Type II	1.23%	Max. 2%	2.667	2.541	2.592
Type III	1.14%	Max. 2%	2.538	2.505	2.590
Type IV (Sand)	0.57%	Max. 2%	2.664	2.577	2.638

3.1 Water:

Tape water is used for all experiments.

3.1.a Techniques and Instrumentation:

3.1.a.1 Mix Design: (Alnjili, 2015)

After finishing of all tests for concrete constituent and ensure that all material like water, aggregate, sand and cement are according to specification, the concrete will design with strength

ISRAA UNIVERSITY JOURNAL OF APPLIED SCIENCES
ISSN: 2523-0522
Volume3: Issue1, October , 2019

30 MPa at 28 days age. The job mix will be designed according to Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete (ACI 211.1-91). The design criteria that used in the current study is as:

1. **Compressive strength:** The most strength of normal concrete for general use is 30 MPa for cubic strength and ***25 MPa*** for cylinder strength so the mix will be design for that strength.
2. **Slump:** The most slump of normal concrete for general use is between 25 to 100 mm and the mix is designed for slump around 75 to 100 mm.
3. **Nominal maximum aggregate size:** The nominal maximum aggregate size in the job mix is 25 mm.
4. **Water cement ratio:** The water cement ratio in the job mix is 0.57.
5. **The final average weight for job mix:** The final average weight for the job mix is list in Table (5)

Table (5) : The final average weight for the job mix.

Material	Weight (kg)	Volume (m^3)
Entrapped air	0	0.0150
Water	182	0.1650
Cement	320	0. 1016
Coarse aggregate	1161	0.4519
Fine aggregate	687	0.2665
Total	**2350**	**1.000**

3.1.b Preparation of concrete specimen:

3.1.b.1 Mixing procedure:

The concrete will mix according to Standard Method of Making and Curing Test Specimens in the Laboratory ASTM C 192.

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ISSN: 2523-0522
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3.1.b.2 Curing of hardened concrete:

After 20-40 hour, the hardened concrete will be removed from the molds very carefully to prevent any defect in the samples. After that, the samples will be placed in curing water tank at temperature 21-25 C^0 until the period of testing.

3.1.b.3 Fresh concrete test and sampling:

1. Slump Test according to ASTM C 143: the test was made to measure the workability of fresh test according to the standard Test Method for Slump of Portland Cement Concrete ASTM C 143, the scope of this test is determination of the slump of hydraulic-cement concrete.
2. Sampling of fresh concrete in several molds according to ASTM C 192.
3. Compressive strength According to ASTM C 39 and BS 1881, Part 127.
4. Air content according ASTM C138.
5. The morphology and microstructure of the dried hydrated samples are studied using JEOL JXA 840 A electron Probe micro analyzer SEM. The specimens are coated with a thin film of gold under a vacuum evaporator with cathode rays then analyzed.

4. Results and Discussion

4.1 Effect of HYPR on air content of the concrete

Air content is the controlling factor which affects other aspects of the concrete (i.e. density, compressive strength and workability) (**Qaraman,et al,2016**). ***Dodson, 1990*** believed that adsorbed surfactant molecules at the surface of the bubble form a film, with their polar heads in the water phase. If the molecule is charged, the bubble acquires this charge. The electrostatic repulsion keeps bubbles separated and prevents coalescence. In addition, the ends of the surfactants molecules that protrude into the water are attracted to cement grains. This allows for a coating of calcium salts (the products of cement hydration) to be formed around each air bubble, making it more stable than bubbles formed in plain water **(Algurnon, 2013).**

The results, which presented graphically on figure (1) shows that the entrained air is increased gradually with the surfactant concentration until it reaches a maximum value at a fixed surfactant content. However, the maximum air content is 11.31% on using 0.75 % of the HYPR surfactant by weight of cement.

The efficiency of HYPR as air entraining agent may refer to the electrostatic repulsion between the positive charges on the quaternary nitrogen of HYPR and those on the cement grains, which may enhance the air bubbles separation and stabilize them due to the probable formation of hydrogen bonding between the HYPR hydroxyl group and the silica network (CSH).

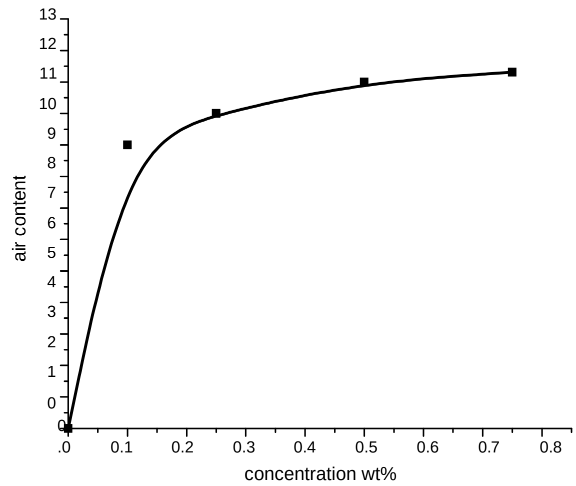

Figure (1): The air entrained by 0.10, 0.25, 0.50 and 0.75% HYPR

4.2 Effect of HYPR on the concrete slump

The slump test is essential for measuring the workability of fresh concrete. The concrete consistency in that specific batch slump test measures the consistency of concrete in that specific batch. It is conducted to test the consistency of fresh concrete. Consistency refers to how much the ease of the concrete flows.

Consistency affects concrete workability. That is, wetter blends are more workable than drier ones, but concrete of the same consistency may vary in workability.

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The recorded data used to observe the relation between quantities of HYPR surfactant and slump loss. The data of slump loss for different quantities of HYPR surfactant as shown in figure (2) the slump loss against the time for different quantities of HYPR. the figure shows that the slump decrease with time. the results are acceptable since the ongoing hydration process produces calcium silicate hydrate which fills the pores between the cement particles and aggregate. As a result, the concrete setting will reduce the concrete fluidity, hence, the slump is reduced too. When observation is done on the content of HYPR, an increase in dosage of the chemical admixture will decelerate the rate of setting of concrete, since HYPR surfactant will help to conserve the fluidity of concrete for a longer time, and hence, reduce the slump loss during the transportation of concrete. The optimum content of HYPR is 0.50 % by cement weight, however, over dosage of HYPR will not lead to significant improvement of concrete slump. As a result, a conclusion is made that HYPR is more effective in retaining the slump of the concrete than the normal concrete.

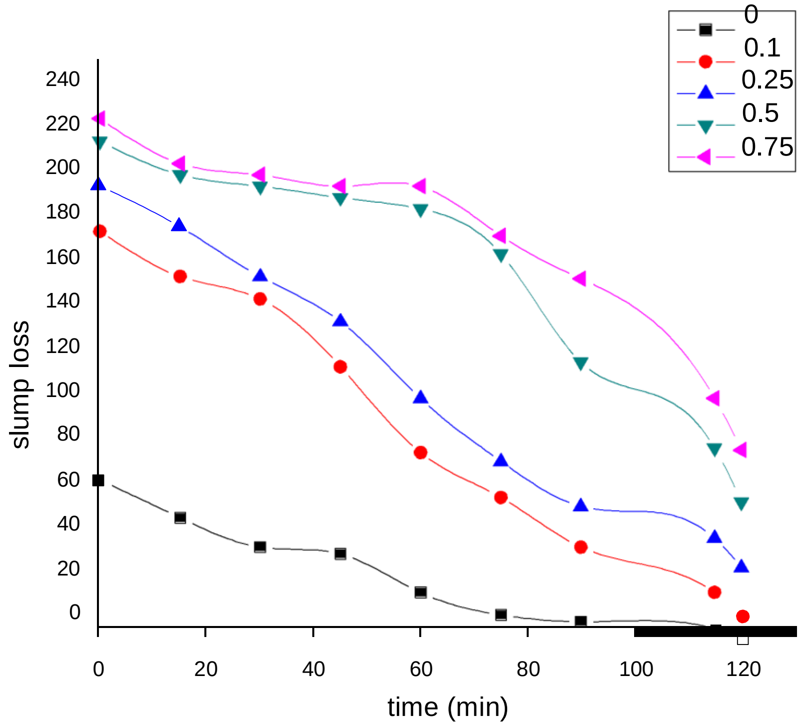

Figure (2): Relations between the HYPR concentration and the slump loss values

4.3 Effect of HYPR on the concrete compressive strength

Compressive strength is a critical criterion in the design of concrete. The properties of concrete are time-dependent, therefore, any test should be conducted at a certain hydration age on concrete. The compressive strength values of concrete with and without HYPR surfactant at different concentrations and different hydration ages (7, 14, and 28 days) were determined. To examining the compressive strength, three specimens of each mix at each hydration time are used. The mean value is considered of the compressive strength of the three specimens at each hydration age. The 7, 14, and 28 days compressive strength of the mixes with 0.10, 0.25, 0.50, and 0.75% of HYPR surfactant by cement weight are shown in Figure (3). The results indicate that 7 days specimens compressive strength is about 75% of 28 days compressive while the 14 days specimens compressive strength reach about 90% of 28 days compressive strength. The compressive strength values of all mixes directly proportional to the progress of the hydration time. This is believed to be due to the progress of the cement hydration reaction. the increment of compressive strength of the concrete specimens with the hydration time is noticed in all cases regardless of the presence or absence of a surfactant or their concentrations. The maximum values of compressive strength are achieved, in all cases, after 28 days of hydration. In addition, Figure (3) shows that the compressive strength was inversely proportional with HYPR dosages, the 7days compressive strength decreased linearly from 20.3 MPa at specimens with 0.10% HYPR to 14.9 MPa at specimens with 0.75% HYPR. The 14 days compressive strength decreased linearly from 25.3 MPa at specimens with 0.10% of HYPR to 18.5 MPa at specimens with 0.75 of HYPR. In the same context, The 28 days compressive strength decreased linearly from 28.4 MPa at specimens with 0.10 % of HYPR to 20.9 MPa at specimens with 0.75% of HYPR.

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This decrease in the compressive strength by increasing the HYPR content can be explained mainly by the increase in the air content of the samples due to the fact that HYPR is an effective entraining agent, these air voids weaken the strength of concrete. (Qaraman & Zuhud, 2018).

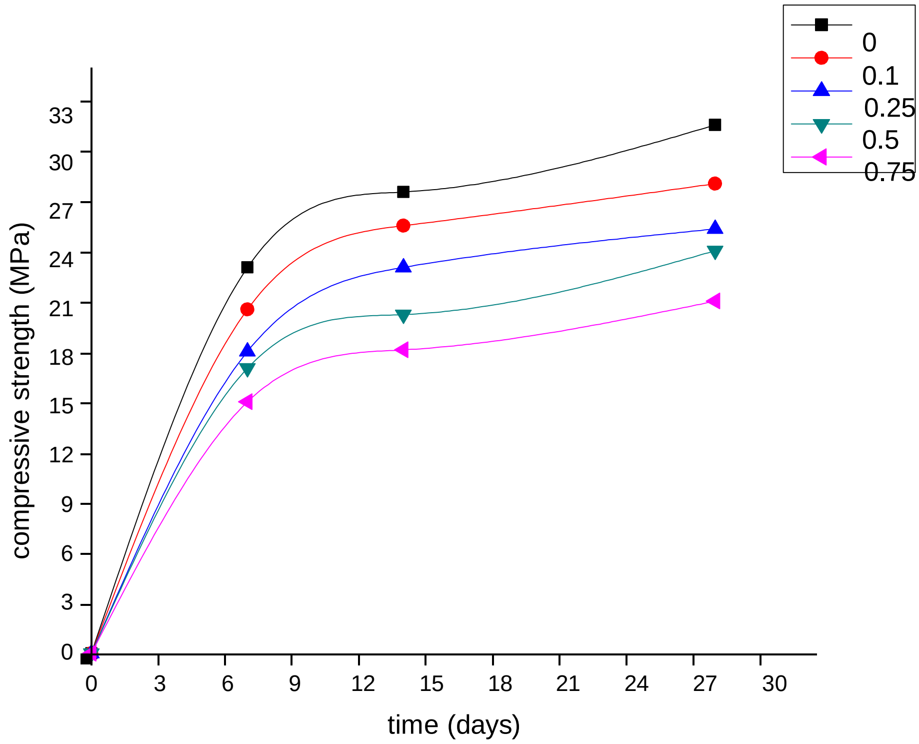

Figure (3): effect of HYPR concentration on the compressive strength

4.4 The morphology and microstructure effect of the addition of HYPR on of the hardened concrete.

The scanning electron microscope (SEM) is a good tool for chemical analysis and imaging in cement pastes and concrete . It's high resolution enables a detailed study the surface topography of the rough surfaces of e.g. the formed calcium silicate hydrate (CSH) and calcium hydroxide (CH). The graphs of the hardened concrete with and without HYPR after 28 days are shown in Figure 4 (a &b). Figure (4-a) shows the hydration products formed in absence of HYPR. CH exist as hexagonal plates and the ettringite needles appears beside the fibrous CSH phase. When HYPR is added an increase in the amount of calcium hydroxide, which has a layered structure, appears beside CSH crystals (figure 4-b) .

On other hand, the structure of concrete with addition of HYPR produces

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a uniform bubbles with small air voids system (80.41 µm) it appear as a more compact system. These results may indicate that HYPR surfactant makes a uniform air void system which construe the decrease of the compressive strength, these results are great confirm previous findings (Qaraman ,2016).

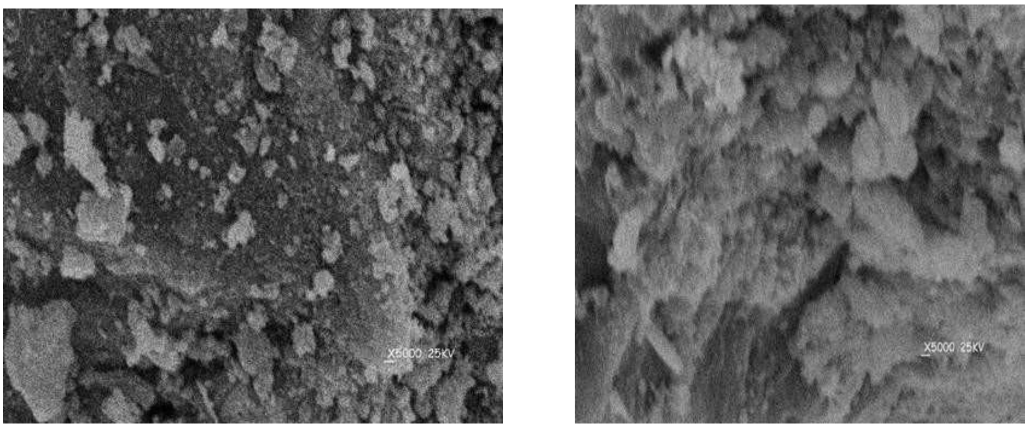

Figure (4): SEM of hardened concrete after 28 days hydration (X = 5000).
a) Without HYPR b) With 0.02% HYPR

5. Conclusion:

The following conclusion were obtained from the experimental observation:

a. The addition of HYPR enhanced the workability and reduced slump loss problem of concrete.
b. The addition of HYPR increase the slump without any segregation.
c. The air content adversely affected the compressive strength which weaken the strength of the concrete.
d. The air content increase by increasing HYPR concentration.
e. 0.5% HYPR by cement weight is the optimum content of HYPR ; the using of higher dosage does not show any effective improvement to the slump.

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