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EVALUATION OF A TREATED CARBOHYDRATE WASTE AS A WATER REDUCING ADMIXTURE FOR CONCRETE

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ABSTRACT

The industrial wastes produced from the manufacture of starch and processing of carbohydrate food represent the most difficult environmental problem that chemists have to treat. For the contribution in the environmental protection, this paper presents results from a study aimed at better understanding of the effects of starch as colloidal admixtures (antiwashout admixture) on concrete properties. Basic hydrolysis of incorporated starch (mainly extracted from carbohydrate waste) followed by neutralization with calcium formate was evaluated, by studying fresh concrete properties such as air content and setting time as well as hardened concrete properties such as compressive strength. Also, the effect of mixing of starch with the commercial sodium dodecyl benzene sulfonate as a typical air-entraining agent was examined.

Key Wards: Starch, antiwashout admixtures, Concrete, air-entraining admixtures, Compressive strength, Setting time and commercial sodium dodecyl benzene sulfonate.

INTRODUCTION

Most colloidal (antiwashout) admixtures are water-soluble polymers that have been incorporated into concrete intended for under water placements and repairs, and implemented in production of extremely workable and flowing concrete. They have also been used to enhance resistance to sagging of shotcrete and produce bleed-free cement grouts for filling post-tensioning ducts.

Ramachandran (1984) categorized pumping aids and antiwashout colloidal admixtures into five classes according to their physical actions in concrete as follows:

Class A: Water-soluble synthetic and natural organic polymers. Materials of this class include starch, cellulose ether derivatives, and polyethylene oxides.

Class B: Organic water-soluble flocculants that become adsorbed onto cement grains, materials of this class include styrene copolymers with carboxyl groups, synthetic polyelectrolytes and natural gums.

Class C: Emulsions of various organic materials that enhance interparticle attraction, among the materials belonging to class C are acrylic emulsions and aqueous clay dispersions.

Class D: Water-swellable inorganic materials that increase the water-retaining capacity of the paste, such as bentonites and silica fume.

Class E: Inorganic materials of high surface area that increase the content of fine particles in paste, such as fly ash, and hydrated lime.

Cellulose derivatives are often used in conjunction with melamine-based as high range water reducing admixtures because of their incompatibilities with naphthalene-based high range water reducing admixtures [**Kawai (1987); Neeley (1988); Khayat (1991) and Kawai & Okada (1989)**] reported that the use of hydroxypropyl methyl cellulose in an aqueous solution with pH 13 and naphthalene-based high range water reducing admixtures causes the formation of a gel resulting from a chemical reaction between the two admixtures.

Yamamuro (1999) showed that a polysaccharide derivative containing an ionic functional and a hydrophobic group increases the viscosity of cement suspensions. In the shotcrete process, **[Ghio & Monteiro (1998) and Ghio et al., (1994)]** showed that concretes formulated with polysaccharides are easier to pump and spray at high shear rates than unadmixed concrete. Moreover, concrete is more cohesive and viscous at low shear rates. **[Tanaka et al., (1996)]** patented an additive that contains at least one sulphated polysaccharide to improve fluidity and workability and to supply higher final compressive strength. **[Hayakawa & Soshiroda (1985)]** reported that cellulose ether improves binding between cement matrix and aggregates. Also, **[Ferrari et al., (2000)]** mentioned that both adsorption and steric stabilization were the main factors determining the performance of polycarboxylate superplasticizers. The dispersing efficiency of these polymers is a function of carboxylate groups/ ester side chains, which affects a balance between adsorption and steric effects.

Franc Švegl et al., (2008) studied the influence of γ-aminopropyltriethoxy-silane (APTES), and *N*-*β*-aminoethyl-γ-aminopropyltrimethoxylsilane (AEAPTES) on macroscopic properties of fresh and hardened cement pastes and mortars prepared from ordinary Portland cement. The mixing ability of aminosilane substances with water is an advantage in comparison to other types of organofunctional silanes when used as an admixture to the cement system. This enables direct blending with water and cement and homogeneous distribution of aminosilane molecules through the bulk of the cement material. The highly polar amine and alkoxide groups of aminosilane molecules exhibit strong chemical interactions with cement matrix which are reflected in modified macroscopic properties of the cement system.

Cordeiro et al., (2008) showed that the use of sugar cane bagasse ash (SCBA), which is generated as a combustion by-product from boilers of sugar and alcohol factories, as a partial Portland cement replacement can improve some properties of cementitious materials. They investigated the pozzolanic and filler effects of a residual SCBA in mortars. Initially, the influence of particle size of SCBA on the packing density, pozzolanic activity of SCBA and compressive strength of mortars was analyzed. In addition, the behavior of SCBA was compared to that of an insoluble material of the same packing density. The results indicate that SCBA may be classified as a pozzolanic material, but with its activity depending significantly on its particle size and fineness.

Burak Felekoğlu & Hasan Sarıkahya (2008) mentioned that in self-compacting concrete mixture (SCC) design, polycarboxylate-based superplasticizers (PC-based SPs) usually guarantee the initial workability. PC-based SPs are the copolymers of chemical structures which have the potential to be modified to improve their performances. However, the time dependent workability of mixtures principally depends on the chemical structure of PC-based SPs and its compatibility with cement. The results showed that, from the viewpoint of chemical structure, workability retention performance of PC-based SPs could be manipulated by modifying the bond structure between main backbone and side-chain of copolymer.

John Dransfield (2003) reported that admixtures are chemicals, added to concrete, mortar or grout at the time of mixing, to modify the properties, either in the wet state immediately after mixing or after the mix has hardened. They can be a single chemical or a blend of several chemicals and may be supplied as powders but most are aqueous solutions because in this form they are easier to accurately disperse into. and then disperse through the concrete.

EXPERIMENTAL

Concrete Materials:

(1) Ordinary Portland cement (OPC)
(2) Aggregate [Sand and Gravel]
(3) Clean tap water for curing

Table (1): The chemical analysis of the OPC.

Property	Chemical Analysis%
Moisture	0
Loss of ignition	2.0
SiO_2	22.0
Al_2O_3	8.3
CaO	58.0
MgO	2.4
Fe_2O_3	2.8
SO_3	2.5
Na_2O	0.4
K_2O	0.3

Table (2): Physical properties of sand and gravel.

Property	Test results for Sand	Property	Test results for gravel
Specific gravity	2.5	Specific gravity	2.5
Bulk density (t/m^3)	1.585	Bulk density (t/m^3)	1.759
Fineness modulus	2.3	Nominal max. (mm)	20
Clay, silt and fine dust % (by volume)	2.8	Crushing value %	11.1%
T.D.S.	0.06%	T.D.S.	0.03%

Table (3): Concrete mix design.

Cement (kg)	**Sand (kg)**	**Gravel (kg)**	**Water/cement Ratio**
310 kg/m^3	715	1215	Variable to have a slump 11 to 12 cm.
Cement/aggregate ratio		1 : 6.2	
Sand/gravel ratio		1 : 1.7	

Chemical Materials:

(1) Carbohydrate waste (mainly from starch) $\{C_6H_7O_2\,(OH)_3\}_n$

Starch, as obtained from the food waste, contains 2% vegetable oil, 3% inorganic salts and 50 % water. In the extraction of starch, the raw material (food waste) is ground with water; the resulting slurry is filtered off to remove coarse tissue fragments, and a suspension of starch granules is obtained. The granules are collected by centrifuging and drying at 90°C before utilization.

Composition of Starch:

Amylose is the smaller of the two polysaccharides which make up starch, and it is a linear molecule comprising of (1-4) linked alpha-D-glucopyranosyl units; there is a small degree of branching by (1-6) alpha linkages as shown in Figure 1. The water soluble amylose molecule contains 100- 1000 glucose units.

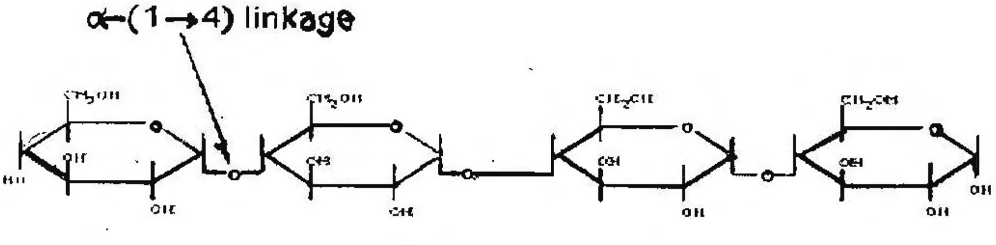


Fig. (1): Amylose molecule

Amylopectin is the larger of the two components, and it is highly branched with a much greater molecular weight; its structure contains alpha-D-glucopyranosyl units linked mainly by (1-4) linkages (as amylose) but with a greater proportion of (1-6) linkages, which gives a large highly branched structure. Amylopectin is much larger than amylose and contains about 500 - 5000 glucose units, and it is insoluble in water as amylose.

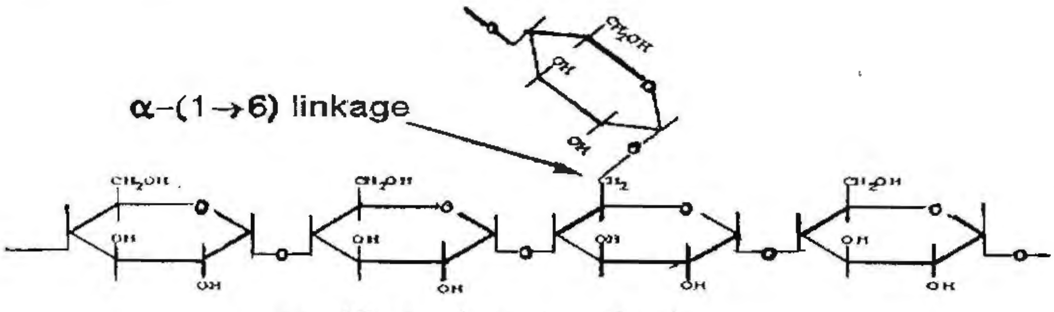


Fig. (2): Amylopectin molecule

Acid treatment of carbohydrate waste is undesirable because the use of hydrochloric acid or sulphuric acid increases the chloride and sulphate ions concentration which affects the concrete properties. Basic hydrolysis is better because it gives quick results in few minutes and does not require any high technology. It was found that the rate of hydrolysis increased by increasing the concentration of the used alkali. High concentration of the alkali is reflected on the viscosity of the dispersing agents and on the pH value.

Hydrolysis of starch waste using 0.8N NaOH was carried out as follows: In a five liter conical flask, 60 gm of starch waste were added to 600 ml of water and 340 ml 0.8 N NaOH solution with continuous stirring for 15 min. at 45 – 50°C in a water bath until a gelatinous solution becomes clear (the pH of this solution is 9). Then, 12 ml of 35% formaldehyde solution was added to prevent fermentation and spoiling of the additive caused by growth of bacteria. This hydrolysis leads to the formation of lower molecular weight polymers containing from 5 to 30 glycoside units.

(2) Calcium formate $(HCOO)_2Ca$

20 gm of powdered $CaCO_3$ were added slowly and in portions, with continuous stirring for 10 min, to 40 ml of formic acid 98%. The mix was left for 2 hours to get rid of the CO_2 produced. The white paste of calcium formate obtained was dried at 105^0C for 3 hours. The produced calcium formate has a melting point= 300°C, it is soluble in

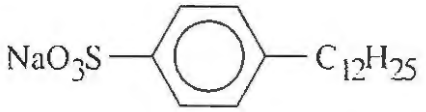
water (Solubility = 160 g/ 1000 g water at 20 °C), its specific gravity = 2.023, and pH = 6 .

Neutralization of the basic hydrolysis product of starch by using Calcium formate

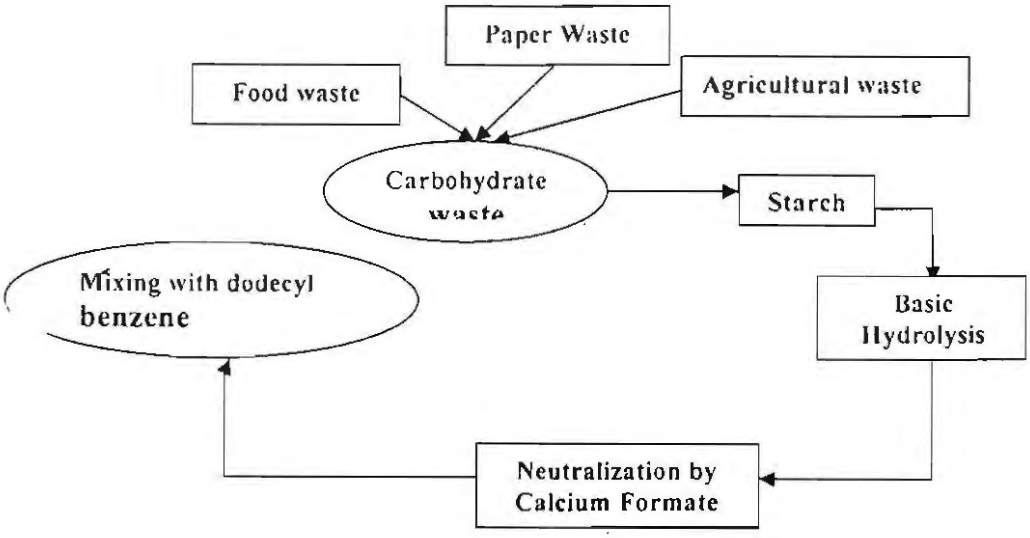
80 ml of formic acid 98%, 40 gm of powdered $CaCO_3$ and 40 gm of starch were simultaneously added with stirring for 15 minutes at room temperature. The produced white emulsion is soluble in water. Using calcium formate in chemical treatment of starch was achieved after detailed studies made to determine the effectiveness of calcium formate as chloride-free accelerating admixture for concrete.

(3) Sodium dodecyl benzene sulphonate

This material is a basic surfactant used in a variety of industrial and domestic detergents. It is a light yellow viscous liquid. soluble in water. Its pH = 8 and has a specific gravity = 1.04.



The neutralized hydrolysis product of starch was finally mixed with Sodium dodecyl benzene sulphonate as indicated in the following scheme



Program of studying the physical properties of concrete containing the carbohydrate waste

Admixture type	Treated carbohydrate waste (starch) trial mixes
Cement content (kg/m^3)	310 kg/m^3
Admixture dose (% by mass of cement)	0.01, 0.02, 0.03 and 0.04
Slump value	11-12 cm
Water content (W/C)	Varied to reach 11-12cm slump
Concrete tests	Fresh (setting time and air content%) Hardened (compressive strength)
Age of hydration (days)	1, 3, 7, 28 and 90

RESULTS AND DISCUSSION

Preliminary investigations were first made to evaluate the influence of hydrolyzed starch waste by sodium hydroxide, followed by neutralization with calcium formate on slump flow, air content, setting time and compressive strength of concrete. Then, the work is concerned with mixing of the treated starch waste with commercial sodium dodecyl benzene sulfonate as a typical air-entraining agent in order to enhance the workability requirements that lead to an increase in the yield of the mix considered to be the economic target. Tables (4 and 5) show the strength results and mix proportions for the used materials.

Table (4): Strength results and mix proportions for different % of the used admixture (Treated Starch Waste).

Additive (%)	**W/C ratio**	**Air content (%)**	**Compressive strength (kg/cm²)**				
			1 day	3 days	7 days	28 days	90 days
Control	0.6	3	80	140	210	270	285
0.01%	0.54	3.7	120	185	250	305	315
0.02%	0.53	3.5	130	185	240	310	330
0.03%	0.51	3.2	140	210	280	330	346
0.04%	0.55	3.6	110	170	230	295	310

Table (5): Strength results and mix proportions for the 0.001% dodecyl benzene sulphonate and the mix compared to the control

Admixture type	W/C ratio	Air content (%)	Compressive strength (kg/cm²)					Yield value (%)
			1 day	3 days	7 days	28 days	90 days	
Control	0.6	3	80	140	210	270	285	0
mix	0.49	15	85	160	235	290	310	8
0.001 % dodecyl benzene sulphonate	0.56	19.5	75	115	200	260	270	10

Mode of action of starch and calcium formate:

Natural polymeric colloidal admixtures include a variety of products capable of enhancing the viscosity of concrete. Since colloidal admixtures increase the cohesion of cement-based systems in general, they can also function as anti-washout admixtures for underwater concreting through a combination of several effects depending on the concentration of the used polymer. Three contributing mechanisms were illustrated which may be summarized as water adsorption, association and entanglement.

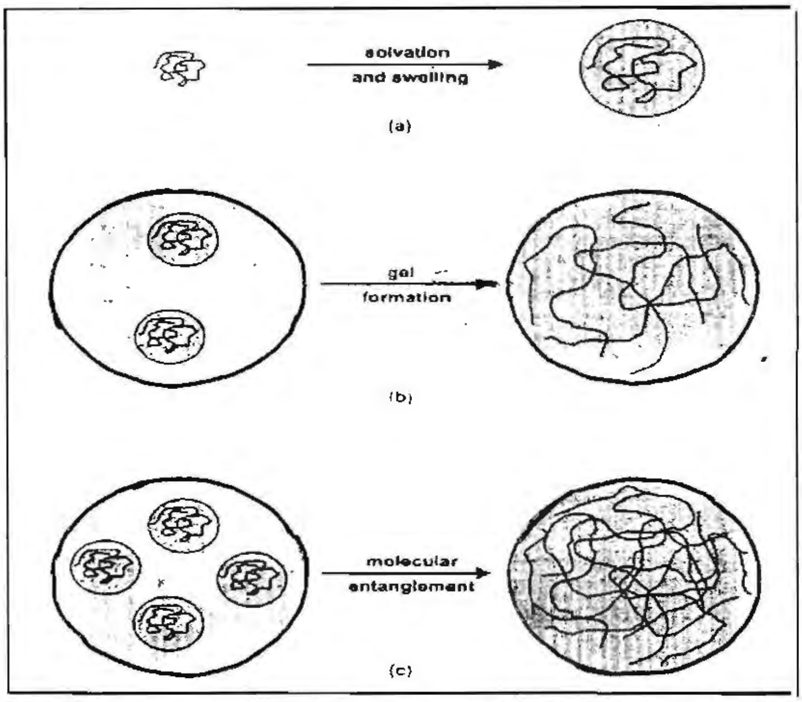


Fig. (3): Schematic illustration of the mechanisms contributing to the function of colloidal admixtures (a) Water adsorption and retention (b) gel formation (c) molecular entanglement

It is often noted that the increase in workability produced by the addition of a water-reducing admixture, can be made without the loss of cohesion. It is believed that during the pumping, casting or even consolidation of the concrete mix, the entangled chains of the polymer can disaggregate and align in the direction of the flow which leads to a decrease in the apparent viscosity with improvement in flowability and spreadability of concrete which will be reflected on decreasing water-cement ratio with increasing workability.

In addition, long chain polymeric colloidal admixtures, such as starch, cellulose derivatives and gums, may be adsorbed simultaneously onto neighbouring cement particles through the different functional groups present in the back bone of the polymer (for example OH, CH_2OH, -O- linkage) forming a bridged structure. Thus reduce the risk of separation of concrete constituents (segregation), reflecting on the increase in the compressive strength results with age of concrete compared to the control mix.

Calcium formate is a soluble organic compound which can be used to offset the retarding effects of water-reducing admixtures or to provide noncorrosive accelerators. In the absence of calcium formate, the sulphate ion concentration (from gypsum) normally diminishes rapidly due to the reaction between gypsum and C_3A phase to form ettringite. which is useful to slow down the flash set by C_3A; i.e. delay of the setting time.

The following reaction describes the ettringite formation.

$$\mathbf{C_3A + CaSO_4 + 32\ H_2O \rightarrow C_3A.3CaSO_4.32H_2O(ettringite)}$$

But in the presence of the admixture, calcium formate reacts with C_3A as follows:

$$\mathbf{(HCOO)_2\ Ca + C_3A + x\ H_2O \rightarrow C_3A.\ (HCOO)_2\ Ca\ .\ x\ H_2O}$$

The way in which calcium formate and calcium chloride operate is not fully understood, but it is clear that the mechanism involves an acceleration of C_2S and C_3S hydration. It has been proposed that the initial products of cement hydration form a sort of 'membrane' which acts as a restraint to the diffusion process which in turn leads to the "dormancy period".

It seems likely that the chloride ion (and it can be proposed that also formate ion) is able more easily to penetrate the pores of the restraining layer allowing the diffusion process to be more rapid. Hence a decrease in the total porosity of the system which in turn leads to an increase in compressive strength compared to the control mix.

Influence of water / cement Ratio:

Figure (4) shows the influence of treated carbohydrate waste (starch) on W/C ratio compared to control mix. It is clear from the results that addition of different percentages of the admixture to the mixes leads to a considerable water reduction, and that the marked reduction in the W/C ratio was attained by using 2 % of the admixture (optimum amount).

Figure (5) shows the influence of the mix with 0.001 dodecyl benzene sulphonate sulphonate formaldehyde (optimum amount) on W/C ratio. Analysis of the data shows that the mix leads to the least reduction in W/C ratio, which is probably reflected on the compressive strength.

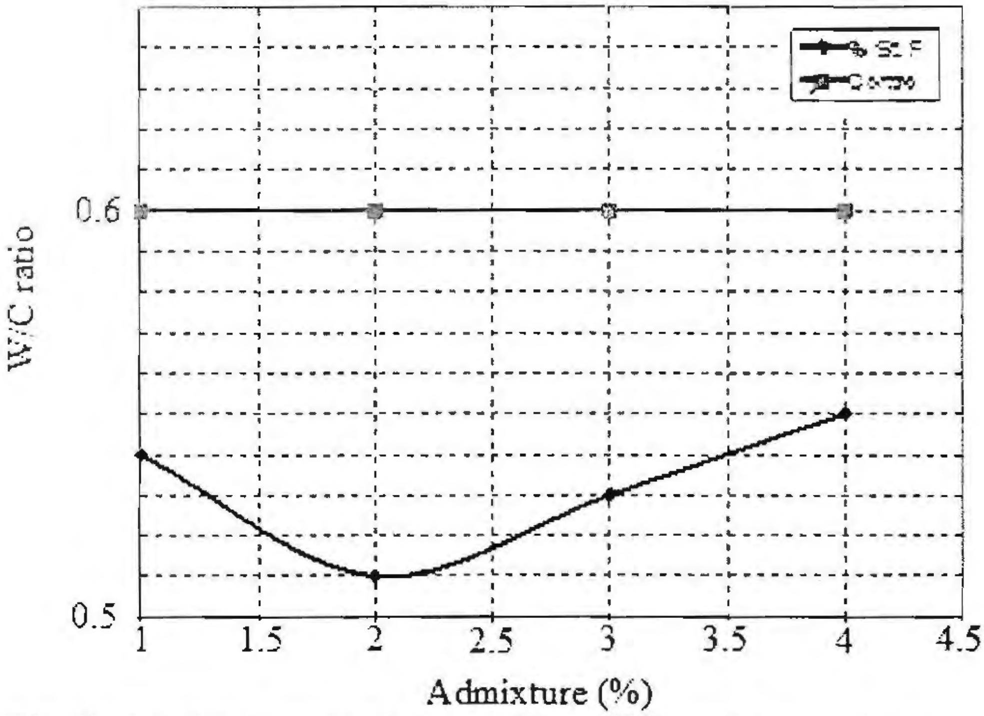


Fig. (4): Relation between admixture (%) and W/C ratio of concrete.

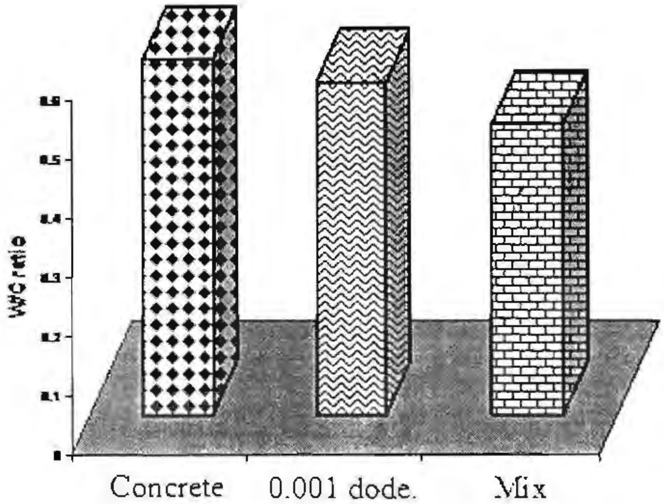


Fig. (5): W/C ratio for concrete containing 0.001 sodium dodecyl benzene sulphonate formaldehyde and the mix compared to the control.

Influence of air content:

Figure (6) shows the air content of concrete with varying percentages of the treated carbohydrate waste (starch). The results clearly show that by increasing admixture percentage, the air content decreases up to 2%. But adversely, by increasing percentage more than 2%, the air content increases up to 4%.

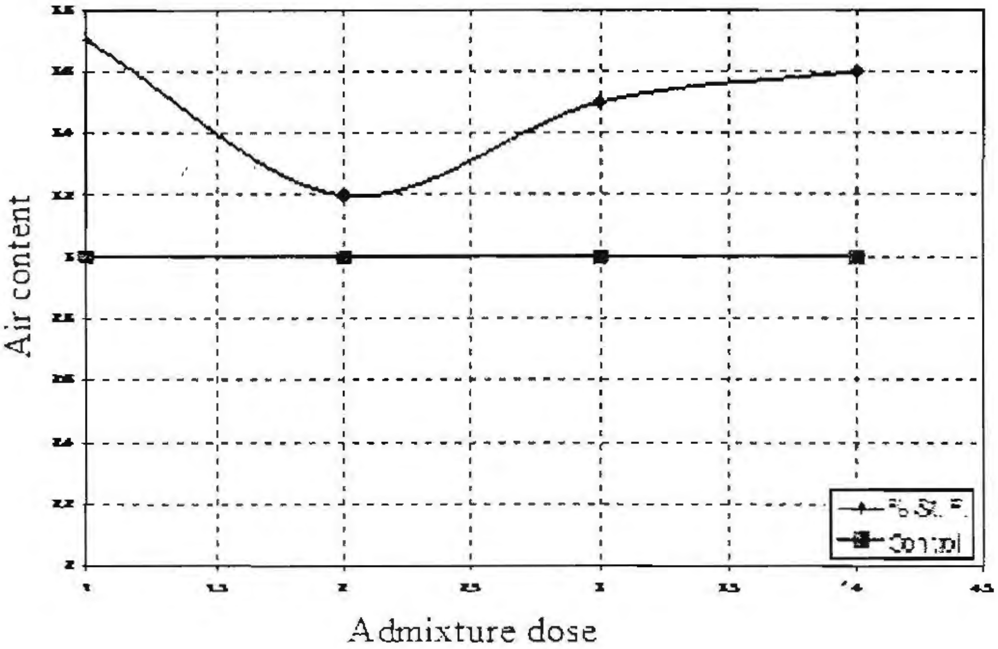


Fig. (6): Relation between Admixture % and air content of concrete specimens.

Figure (7) shows the air content results of the mix with 0.001 sodium dodecyl benzene sulphonate formaldehyde (optimum amount). Results illustrate that the air content of the mix is lower than that containing 0.001 sodium dodecyl benzene sulphonate formaldehyde but higher than the control indicating thus increase in the yield value of the concrete.

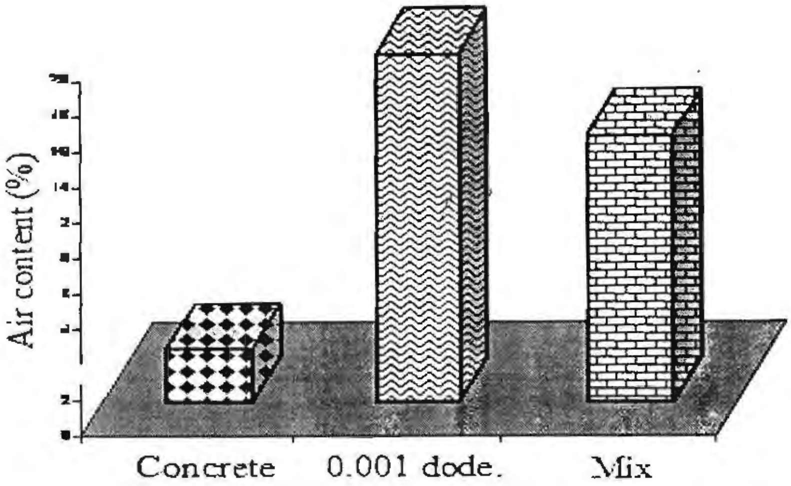


Fig. (7): Air content % for concrete containing 0.001 sodium dodecyl benzene sulphonate formaldehyde and the mix compared to the control.

Influence of admixtures on compressive strength:

Since the results of air content and water/ cement ratio indicate that the admixture content of 2 % gives the lowest water/ cement ratio and a comparable air content value between the concrete control mix and concrete containing 0.001 sodium dodecyl benzene sulphonate formaldehyde, it can be concluded that 2% is the optimum amount of additive for use in concrete and these results are confirmed by the compressive strength data as shown in Figure (8) since the compressive strength data are considered to be a good support to the results of the air content.

This investigation also includes a comparison of compressive strength results of concrete containing 0.001 sodium dodecyl benzene sulphonate formaldehyde and the mix compared to the control. The results illustrate that the mix gives off the highest compressive strength values at all ages of hydration as shown in Figure (9).

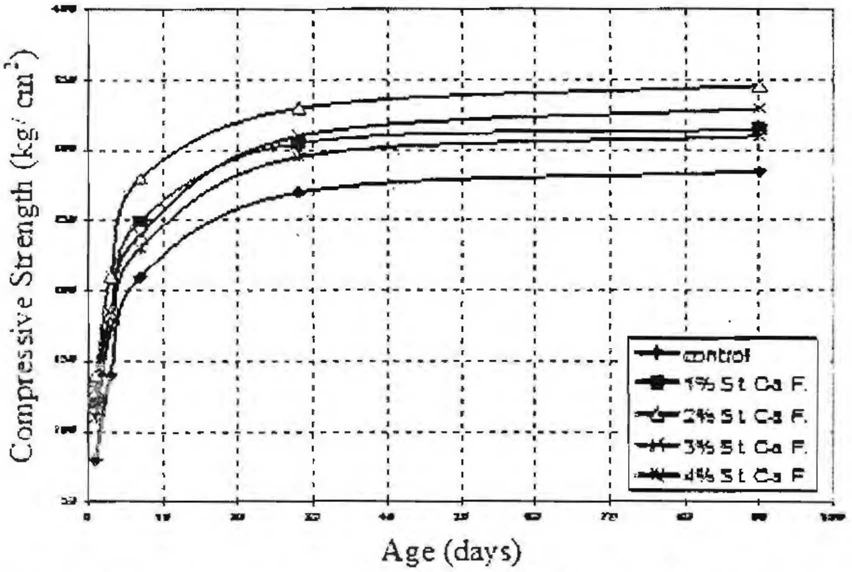


Fig. (8): Relation between compressive strength and age of hydration.

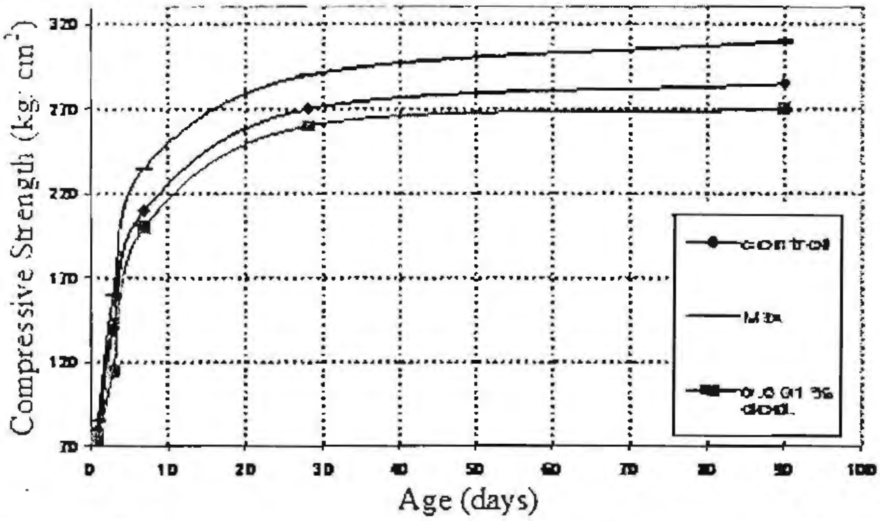


Fig. (9): Relation between compressive strength and age of hydration.

In addition, the results of figure (10) indicate that the yield value (increase in volume) of concrete is increased due to the considerable volume of the entrained air for the given weight of mix ingredients as well as a marked increase in the workability, i.e. suitable requirements to produce the lightweight and filled concrete types. Evidently, the results indicated that the better yield with comparable compressive strength for concrete could be achieved by using the mix of sodium dodecyl benzene sulphonate formaldehyde with the treated carbohydrate waste.

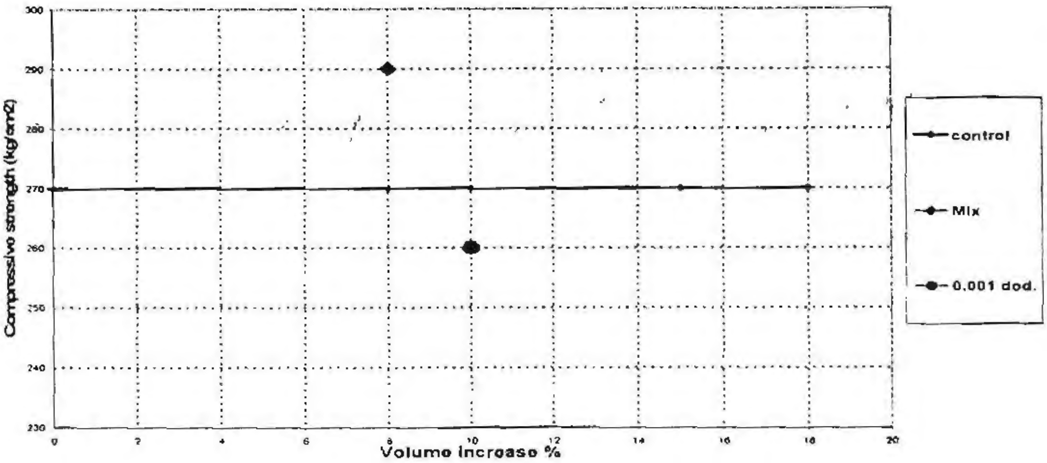


Fig. (10): Relation between compressive strength after 28 days and volume increase (yield) for concrete containing 0.001 sodium dodecyl benzene sulphonate formaldehyde and the mix compared to the control.

Influence of setting time:

Figure (11) shows the penetration resistance of concrete versus time by using proctor needle, to show the effect of admixtures on the setting characteristics of concrete. For concrete mixes which contain the optimum percentage of sodium dodecyl benzene sulphonate formaldehyde and the mix it can be concluded that these admixtures are acting as accelerators compared to the control.

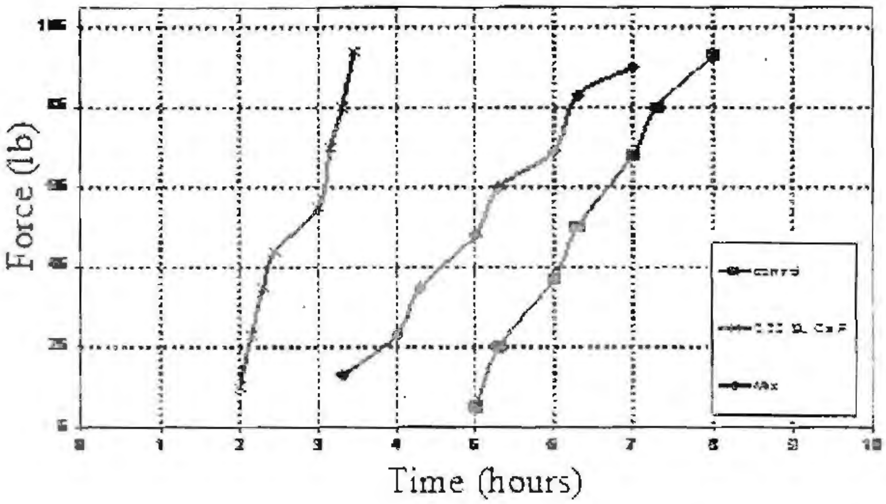


Fig. (11): Relation between force and time for 0.001 concrete containing sodium dodecyl benzene sulphonate formaldehyde and the mix compared to the control.

CONCLUSION

The main conclusions derived from the results of this study can be summarized as follows:

1. The use of colloidal admixtures such as treated carbohydrate waste (starch) can greatly enhance the properties of fresh and hardened concrete: i.e. a more uniform quality concrete can be secured with improvements in mechanical properties.
2. Mixing of the treated carbohydrate waste with commercially produced sodium dodecyl benzene sulphonate, as a typical air entraining agent, increases the yield value of the concrete by maintaining the compressive strength higher than the control mixing also reduces the acceleration of setting time produced by the dodecyl alone.
3. Since the use of carbohydrate waste is a new trend in concrete technology, further research is needed especially for long-term conditions and also studying the resistance against the attack of aggressive solutions.

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Starch, Concrete, air-entraining admixtures,Compressive strength, sulfonate.

تقييم مخلفات المواد الكربوهيدراتية المعالجة كيميائياً والمستخدمة كإضافات مخفضة للمياه للخرسانة

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تعتبر المخلفات الناتجة من صناعات النشا والمواد الكربوهيدراتية الغذائية من المشاكل البيئية الصعبة والتى يحاول الكيميائيين الوقوف عليها ومعالجتها ، وللمساهمة فى إيجاد حل لهذه المشكلة يهدف هذا البحث الى عرض وفهم النتائج التى توضح تأثير إستخدام مخلفات النشا كإضافات غروانية على خواص الخرسانة. فقد تم دراسة التحلل القاعدى للنشا الناتج من المخلفات الغذائية ثم عمل عملية تعادل بإستخدام فورمات الكالسيوم ثم تقييمها كإضافات للخرسانة عن طريق دراسة خواص الخرسانة الطازجة مثل محتوى الهواء ومعدل الهبوط وزمن الشك وايضاً دراسة خواص الخرسانة المتصلدة كإختبارقوة الإنضغاط. ايضاً تم دراسة تأثير خلط النشا مع مادة صوديوم دوديسيل بنزين سلفونات التجارية كإضافات الهواء المحبوس على الخرسانة.