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## The Mode of Action of LM and SLBS Surfactants on the Properties of Cement Pastes

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The Physiochemical and Mechanical Properties of cement pastes containing synthetic surfactants as air entraining agents are investigated by adding different percentages of each of the nonionic surfactant Luramide 11 (LM) and the anionic surfactant Sodium lauryl benzene sulfonate (SLBS) to some Portland cement pastes. The influence of the different surfactants concentrations and the mixing times on the air content of the pastes and accordingly the bulk density, compressive strength and microstructure of the hardened cement specimens is discussed. The optimal level of factors to achieve the desired goals is determined. The results show that LM is more preferable than SLBS in most cases.

### Keywords:

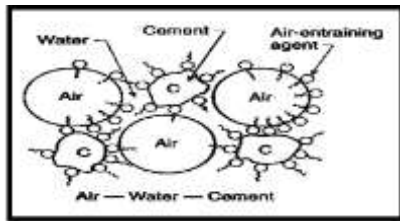
Air-entraining admixtures,  
Density,  
Compressive strength,  
XRD,  
Luramide 11,  
Sodium lauryl benzene sulfonate,  
surfactant.

## 1. Introduction:

It is well known that the pore structure of hardened cement pastes strongly influence their physical properties. The presence of an air-entraining agent (AEA) not only improves workability, but also enhances its freeze-thaw resistance (Lea's, 2004). Du and Folliard (2005) noted that there is a minimum dosage of AEA required to entrain air in the concrete. Rosen (2004) reported that the formed air bubbles in cement pastes are unstable and have limited lifetimes. Therefore, surfactants as AEAs are used in many cases to entrain air bubbles and stabilize them in the fresh cement pastes. Lea (1971) and Zhang (2001) suggested that air entraining surfactants operate at the air-water and solid-water interfaces (Figure 1). They help reducing surface tension of water, thus promoting dispersion and bubble forming. Leslie

and Qingye (2004) concluded that the addition of AEA increased the air content up to a saturation level, above which no further increase in air content was observed. Qaraman (2016) and Algurnon (2013) stated that a number of factors influences entrained air. Examples of such as factors include the duration of mixing and the nature and concentration of the surfactants used as air-entraining agents.

Concerning the mixing time, Patrick (1968) reported that duration of stirring affects the air void system in such a way as to cause an increase in the air content and the specific surface area of the voids as the mixing time increases. In addition, Yang (2012) observed that mixing a longer time could entrain more air in fresh cement pastes by applying more work on it.



**Figure 1** Interaction between air bubbles and cement particles

Jolicoeur et al. (2003) concluded that the processes of air entrainment and air void stabilization in cement pastes depend on the surface activity of the surfactant available in solution. Dodson (1990) claimed that absorbed surfactant molecules at the surface of the bubble form a film with their polar heads in the water phase. If the surfactant molecule is charged, the bubble acquires this charge, hence the electrostatic repulsion keeps bubbles separated and prevents coalescence.

The objective of this work is to study the effect of both the mixing time and the nature and concentration of the two different surfactants LM and SLBS on the air content of cement pastes and accordingly on the bulk density and the compressive strength of the cement specimens. In addition, the microstructure of the hardened cement samples has to be examined using X-ray diffraction and SEM techniques.

## 2. Experimental:

### 2.1. Materials:

- Portland cement of mark CEM I 52.5N obtained from El-Arish cement factory. Its chemical composition is given in Table 1.
- Luramide 11, a nonionic surfactant, and Sodium lauryl benzene sulfonate, an anionic surfactant, are supplied from Merck and used as such.

**Table 1** Chemical composition of the used ordinary Portland cement (OPC)

Oxide (%)	OPC
SiO <sub>2</sub>	22.12
Al <sub>2</sub> O <sub>3</sub>	5.56
Fe <sub>2</sub> O <sub>3</sub>	3.69
CaO	62.87
Na <sub>2</sub> O	0.26
K <sub>2</sub> O	0.11
Cl <sup>-</sup>	0.02
MgO	2.36
SO <sub>3</sub>	0.91
Free CaO	0.92
Ignition Loss	1.22

## 2.2. Techniques and Instrumentation:

### 2.2.1. Paste preparation:

The cement specimens are prepared by dissolving different concentrations of each of the two surfactants mentioned above in 650 g H<sub>2</sub>O then adding to 1500 g cement. The water to cement ratio (W/C) is 0.43 as recommended (Jolicoeur et al., 2003). The percentages of the surfactants used range from 0.005 to 0.080 % by weight of cement.

The mixing are carried out under continuous and vigorous stirring for about three minutes (Jolicoeur et al., 2003). After complete mixing the resulted pastes is poured into (12 ×4 ×4 cm<sup>3</sup>) moulds. The moulds are kept at about 100% relative humidity at room temperature for one day. The hardened cement pastes are then removed from the moulds after they attained the final setting and cured under water for the rest of the hydration ages (up to 360 days).

### 2.2.2. Compressive Strength:

Three specimens of each mix at different hydration times (3, 7, 28, 90 and 360 days) are used for examination the compressive strength of the pastes. The mean value of the three specimens at each hydration age is considered as the determined compressive strength. The strength test machine used is of point load taster (20063 cemasco S/N-Controls) type, Milano-Italy.

### 2.2.3. Stopping of hydration:

This is performed after doing the compressive strength test by taking about 10 g of the crushed hardened pastes and putting into a beaker containing 100 ml of acetone/ethyl alcohol (1:1 by volume) to stop the hydration process. The mixture is stirred for 0.5 hr. The residue is filtered off, washed with ethanol and dried at 50° C for about 24 hrs. The dried samples are then stored in a desiccator for the following physico-chemical analysis.

### 2.2.4. Determination of the bulk density of the cement pastes:

The bulk density is determined by measuring the weight of the sample in air and under water. The density is then calculated as mentioned in (ASTM Standard C 138-08 – 2008).

### 2.2.5. Determination of the air entrained in the cement pastes:

The percent of air entrained in pastes was determined by the difference in weight of a hardened cement paste in absence and in presence of surfactants by the equation (Jolicoeur et al., 2003):

$$\text{Percent of air entrained} = \frac{A - B}{A} \times 100 \%$$

**Where:**

**A:** The weight of hardened cement paste in absence of surfactant.

**B:** The weight of hardened cement paste in presence of surfactant.

**2.2.6. X-Ray Diffraction analysis (XRD):**

XRD patterns of the samples are recorded by using a Philips X Pert MPD diffractometer using copper target with nickel filter under working conditions of 40-kilo volts and 20 milliampers.

**2.2.7. Scanning Electron Microscopic (SEM) measurements:**

The morphology and microstructure of the dried hydrated samples are studied using JEOL JXA 840 an electron Probe micro analyzer SEM. The specimens are coated with a thin film of gold, under vacuum evaporator with cathode rays then analyzed.

**3. Results and Discussion**

**3.1. Effect of the surfactants on the air content of cement pastes:**

Air content is a controlling factor, which affects many physical and mechanical properties of cement pastes (e.g., bulk density, compressive strength, workability, etc.).

On adding an air entraining surfactant to cement pastes, its molecules are inserted between adjacent molecules at the water surface, the mutual attraction between the separated water molecules is reduced. Lowering the surface tension stabilizes the bubbles against mechanical deformation and rupture, making it easier for bubbles to be formed.

The values of the air content entrained in Portland cement pastes hydrated for 90 days in presence of different percentages of LM and SLBS are determined. It should be mentioned that the content of air entrained in cement pastes show a slight change at the different hydration ages (from 3 up to 90 days). However, the air content exhibits the best value at 90 days of hydration. The results in Table 2 show a gradual increase in the air content with increasing surfactant concentration and reach a maximum value at a concentration of 0.06% and 0.08% for LM and SLBS, respectively.

However, the maximum air content is 8.55% on using the LM surfactant, while it reaches only 7.10% in presence of SLBS. This means that SLBS is less efficient as an AEA than LM. This low efficiency of anionic SLBS

surfactant may be attributed to its sensitivity to the presence of Ca<sup>2+</sup> ions in the pastes media as mentioned in literature Porter (1994), Salloum et al. (2000), and Kun Yang et al. (2007).

On the other hand, the nonionic surfactant LM has the advantage over SLBS because it is not affected by water hardness or pH changes (Rosen, 2004). This may explain the ability of LM to introduce more air in the cement pastes than SLBS.

**Table 2** Values of the air entrained by using LM and SLBS surfactants at 90 days

Surf. conc. (wt%)	0.00	0.005	0.02	0.06	0.08
	% of air entrained				
LM	2.70	6.05	6.44	8.55	8.36
SLBS	4.26	5.60	5.77	6.64	7.10

**3.2. Effect of the surfactants on the bulk density of cement pastes:**

The density of cement pastes is directly affected by the air content, they are inversely proportional to each other. It is found that the density of the hardened cement pastes does not considerably change with the hydration age. The determined density of the hardened control specimen (zero surfactant concentration) and those of the specimens containing LM and SLBS surfactants after 90 days of hydration are shown in Table 3. The results show that the density decreases with increasing surfactant concentration, and reaches its minimum value at 0.08% wt of the surfactant in both cases. It is found that, the density decreases by about 0.3g/cm<sup>3</sup> when the air content is increased by about 14%.

**Table 3** The density of hardened cement pastes with LM and SLBS surfactants at 90 days

Surfactant	0.00	0.005	0.02	0.06	0.08
	ρ (g/cm <sup>3</sup> )				
LM	2.00	1.93	1.88	1.85	1.83
SLBS	2.00	1.91	1.89	1.86	1.85

**3.3. Effect of the mixing time on the air content of the hardened cement pastes in absence and presence of surfactants:**

Mixing time plays an important role in controlling the air content in the cement pastes. The effect of changing the mixing intervals from 3 to 5, 6 and 8 minutes is studied in absence and presence of the surfactants at 0.02% concentration after 90 days of hydration. It is found that changing the mixing time has

no effect on the control pastes (without adding surfactant). Similar finding are reported in the literature (Powers, 1968; Rosen, 2004; Algurnon, 2013). It is supposed that in absence of an AEA, consolidation of the cement pastes will cause most of the air bubbles to make their way to the surface and burst. However, the results obtained in presence of the surfactants Table 4 show that the air entrained content increases gradually with increasing the mixing time intervals then reaches a certain maximum in each case.

This result is in a good agreement with previous studies reported by Bruere (1955) and Yang (2012). It is reported that the duration of stirring affects the air void system in such a way as to cause an increase in the air content. The specific surface area of the voids also increases as mixing time increases.

Where, during prolonged mixing at a constant speed, air content increases rapidly at first and then slowly approaches an upper limit.

**Table 4** Effect of mixing time on the air entrained by 0.02% of LM and SLBS at 90 days of hydration

surfactant	Mixing time (min)	3	5	6	8
	% of entrained air				
LM		6.05	6.50	7.00	7.50
SLBS		5.60	6.30	6.50	6.55

### 3.4. Effect of the surfactants on the compressive strength of the hardened cement pastes:

**Table 5** The compressive strength (N/mm<sup>2</sup>) of hardened cement pastes with SLBS at different ages

Surf. Con. (wt%)	Hyd. Time (day)					
	0	0.005	0.02	0.03	0.06	0.08
3	40.42	41.65	41.56	41.20	40.31	39.86
7	50.38	48.81	44.03	44.90	45.60	45.70
28	68.99	68.56	59.53	58.80	57.03	54.78
90	72.70	74.20	72.49	71.50	64.66	61.04
360	104.00	108.00	101.00	100.40	99.00	93.00

**Table 6** The compressive strength (N/mm<sup>2</sup>) of hardened cement pastes with LM at different ages

Surf. Con. (wt%)	Hyd. Time (day)					
	0	0.005	0.02	0.03	0.06	0.08
3	40.42	44.53	43.00	39.09	38.05	39.71
7	50.38	51.02	49.61	47.85	49.05	47.33
28	68.99	64.41	63.78	56.92	57.81	53.43
90	72.70	66.26	79.19	74.57	71.08	64.48
360	104.00	103.00	138.00	129.00	124.00	96.00

Compressive strength of hardened cement is an important criterion specified in the design of lightweight cement pastes and should be considered equally important as density (Algurnon, 2013). The properties of these pastes are time-dependent, therefore, any test method on the cement pastes should be performed at a certain hydration age.

In this work, the determined values of the compressive strength of Portland cement pastes in absence and in presence of the surfactants LM and SLBS at different concentrations and different hydration ages are given in Table 5. Generally, all mixes show an increase in the values of the compressive strength with increasing hydration time. This increase is believed to be due to progress of the cement hydration with time. In nearly most cases, the compressive strength decreases on increasing surfactants concentration at all hydration ages. This is expected as being due to the increasing percentages of entrained air which may affect the compressive strength values. Also, the SLBS specimens exhibit the highest value for the compressive strength (108 N/mm<sup>2</sup>) at 0.005% surfactant after one year of hydration, while the LM specimens show the highest compressive strength values (138, 129, 124, 96 N/mm<sup>2</sup>) at the other surfactant concentrations (0.02, 0.03, 0.06 and 0.08%, respectively). The optimal LM concentration is thus considered 0.02%.

### 3.5. Effect of surfactants on the phase composition of the hardened cement pastes:

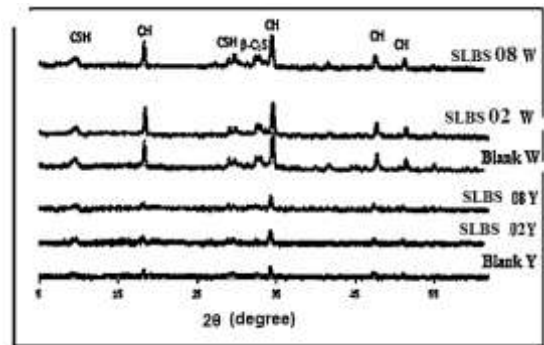
The rates of change in physical and chemical properties of Portland cement pastes depend upon the rates of hydration of the components in cement. Both  $C_3S$  (alite phase) and  $\beta-C_2S$  (belite phase) react with water to form calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). The C-S-H provides most of the strength developed by Portland cement.  $C_3S$  hydration occurs more rapidly than  $C_2S$  hydration. Therefore,  $C_3S$  provides most of the early age strength while  $C_2S$  contributes mostly to the later age strength (Gartner et al., 2002).

The phase composition of the various hardened Portland cement pastes in absence and presence of the surfactants LM and SLBS is examined at the two hydration ages 7 days as an early hydration age and 360 days as a late age of hydration using 0.02 and 0.08% surfactant concentrations applying the X-ray diffraction technique. The reactants ( $C_3S$  and  $C_2S$ ) and products (CSH and CH) of cement hydration, (both for the control mix and on using LM and SLBS) are shown in Figures 2 and 3, respectively. It can be observed that, the intensity of the characteristic peaks of the reactants such as alite and belite phases decreases with increasing the hydration age.

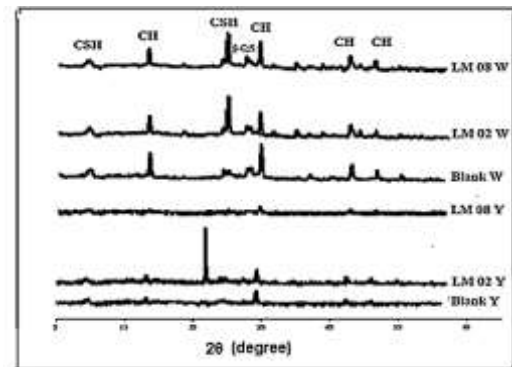
At 7 days, it is found that the intensity of the peaks characteristic of calcium silicate hydrate (CSH) increases on adding either 0.02 or 0.08% LM surfactant compared with the blank and SLBS specimens. This indicates that LM accelerates the hydration of the cement pastes in early ages.

After one year, the peaks characteristic of  $\beta-C_2S$  (belite phase) disappeared completely and converted to the hydration products, calcium silicate hydrate (CSH) and calcium hydroxide (CH). The intensity of the CSH peak increases in the samples containing of 0.02% LM, while in case of 0.08% concentration both CSH and CH peaks remain the same as in the blank. Also no difference is observed between the blank and SLBS specimens.

Hence, it can be concluded that both 0.02 and 0.08 concentrations of LM accelerate the hydration reaction in the early age but after a year only the low dosage 0.02% accelerates the hydration reaction, while the addition of SLBS does not affect the hydration process of the cement pastes.



**Figure 2** X-ray diffraction of hardened cement pastes with and without 0.02 and 0.08 % SLBS at 7 days (W) and 360 days (Y)



**Figure 3** X-ray diffraction of hardened cement pastes with and without 0.02 and 0.08 % LM at 7 days (W) and 360 days (Y)

### 3.6. Effect of surfactants on the microstructure and morphology of the hardened cement pastes:

The scanning electron microscope (SEM) is a powerful tool for imaging and chemical analysis in cement research. With a high resolution and a large depth of focus, it enables a detailed study of surface topography of the rough surfaces of e.g. the formed calcium silicate hydrate (CSH) and calcium hydroxide (CH).

The micrographs of the hardened cement pastes in absence and presence of the surfactants after 7 days are shown in Figure 4 (a, b & c). Figure (4-a) illustrates the hydration products formed in absence of surfactants. Calcium hydroxide appears as hexagonal plates and the ettringite needles exist beside the fibrous CSH phase. Addition of LM (Figure 4-b) shows an increase for calcium hydroxide, which has a layered structure, appears beside CSH crystals.

On the other hand, figure (4-c) shows the micrograph of the cement pastes in presence of SLBS.

The calcium hydroxide hexagonal plates and the ettringite needles beside the CSH phase can be noticed but less condensed than in the case of LM specimens.

Figure 5 (a, b, & c) shows the micrographs of the hardened Portland cement pastes in absence of surfactants and in presence of 0.02% LM and 0.02% SLBS after 360 days hydration. It can be noticed that the hydration products have more compact structure composed of calcium silicate hydrates, which explains the improvement in the strength after year for all mixes.

On other hand, the structure of cement paste with addition of LM produces consistent bubble structure with a uniform small air voids system (70.92  $\mu\text{m}$ ) it seems to be more compact, which resulted in much better strength compared to the other type of mixes. Micrograph of other mixes indicates some empty spaces, SLBS moulds has a large air voids system (103.3  $\mu\text{m}$ ). This could be the reason for these mixes to give lower strength compared to the LM moulds. This indicates that the pore system has a great effect on the compressive strength.

These findings may indicate that LM is more preferable than SLBS as an air-entraining agent because it produces uniform air void system beside its ability to accelerate the hydration reaction. This may help improving the compressive strength of the LM specimens than those obtained on using SLBS as found before.



**Figure 4** SEM of hardened cement pastes after 7 days hydration ( $X = 5000$ ) (a- Without surfactant, b- With 0.02% LM, c- With 0.02% SLBS)



**Figure 5** SEM of hardened cement pastes after 360 days hydration ( $X = 5000$ ) (a- Without surfactant, b- With 0.02% LM, c- With 0.02% SLBS)

#### 4. Conclusion

According to the obtained results, we can conclude that:

1. LM is not affected by the high alkali media of cement and improves the compressive strength indicating its ability to accelerate the hydration reaction.
2. The best compressive strength of LM specimens is attained at LM concentration of 0.02% by weight of cement which reaches 138 N/mm<sup>2</sup> with an increase of 36.6% compared with that of the SLBS specimens.
3. SEM shows that LM causes a uniform distribution of small air voids, which may greatly improve the compressive strength of the pastes.
4. LM is preferred than SLBS to entrain a low dosage of air up to 9%.

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### تأثير كل من المنشط السطحي LM والمنشط السطحي SLBS على خواص العجائن الاسمنتية

#### كلمات مفتاحية:

مواد مدخلة للهواء،  
الكثافة،  
قوة التحمل الميكانيكي،  
حيود الأشعة السينية،  
لوراميد،  
الصوديوم لوريل البنزين أوكتان  
المشبع،  
منشطات السطح.

استخدمت المواد المنشطة للسطح على مدار السنوات الماضية في تثبيت الهواء وانتاج عجائن اسمنتية وخرسانة مهواة وتمتاز الفقاعات الهوائية المثبتة بهذه الطريقة بانها تتفصل عن بعضها بصورة تامة مما يؤدي الى تحسين صفات العزل الحراري والمائي والصوتي.

وتهدف هذه الدراسة الى مقارنة تأثير استخدام تركيزات مختلفة من كل من المنشط غير الأيونى كوكاميد داي ايثيل امين (LM) والمنشط الأنيوني دوداكيل بنزين سلفونيت الصوديوم (SLBS) بالإضافة لتأثير تغير زمن الخلط على محتوى الهواء في العجائن الاسمنتية وبالتالي دراسة تأثيرها على كل من الكثافة ومقاومة الانضغاط والبنية المجهرية للعجائن المتصلدة.

لأجل ذلك تم تحضير عدة مخاليط مكونة من: أسمنت بورتلاندى ومنشطات السطح حيث اضيفت منشطات السطح كل على حدة بنسب مئوية تتراوح ما بين 0.005 الى 0.080 من وزن الاسمنت وقد اذيت هذه النسب في ماء الخلط حيث بلغت نسبة الماء الى الاسمنت 0.43 ثم صببت العجائن المحضرة في قوالب (4سم×4سم×12سم) وحفظت عند درجة حرارة 25م وكذلك عند رطوبة نسبية حوالي 100% لمدة 24 ساعة. بعد ذلك تم فك القوالب وحفظت العينات تحت الماء حتى زمن 360 يوم من بدء الخلط. من خلال النتائج التجريبية المتحصل عليها تبين ان المنشط غير الأيونى (LM) لديه فعالية أكبر من المنشط الأنيوني (SLBS) على ادخال فقاعات هواء متجانسة بالإضافة لتأثيره الإيجابي على مدى التحمل الميكانيكي للعجائن المتصلدة.