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Effect of High Dosage Air-Entraining Admixture Usage on Micro Concrete Properties

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Abstract

In concrete production, because of air entraining admixtures (AEA) are used for a small percentage by weight of cement (in the range from 0.06% to 0.2%), there is a possible risk adding more admixture in concrete than calculated from personnel or equipment's sensitivity errors. In this situation concrete's strength and durability performances are diminishing. In this work, it was investigated the effect of high dosage air entraining admixture usage on mortar properties. It was carried out unit weight, flowability, setting time, air content, compressive strength, flexural strength, ultrasound velocity tests and microstrucural inspections on specimens which were produced with 5 different dosages including control. As a result of experiments, in case of using admixtures with overdose, there would be loss of quality of physical and mechanical properties of concrete, for this reason it is concluded that, there must be some legal regulations using chemical admixtures sensitively.

Key words

Air-entraining, overdose, sodium salt, SEM, XRD, BET

1. INTRODUCTION

Starting with the production, concrete has to endure various durability problems. One of these durability problems is freezing and thawing action whose catastrophic damage can be prevented (or diminished) with air entraining admixtures (AEA). Air entraining admixture allows a controlled quantity of small, uniformly distributed air bubbles to be incorporated during mixing which remain after hardening [1]. Air entrainers are used to develop a large number of small spherical air bubbles in the concrete (diameter in range from 50 to 300 micron [2,3]) which are homogeneous and stable after the mixing process. Compared to capillary pores and gel pores in concrete, entrained air voids are very much larger in size [4] but smaller than the entrapped voids. While water freezes inside the entrapped voids in concrete, it expands about 9% in volume. This volume change enforces internal pressure inside the concrete that exceeds its tensile strength, causing cracking, spalling and eventual disintegration. Providing space for ice in concrete in freezing conditions, entrained air voids help to diminish internal hydraulic pressure and thus protect the hardened concrete. Thus, the entrained air void in concrete is a desirable and intentionally produced void.

Because of air entraining admixtures are used for a small percentage by weight of cement (about 0.1 to 0.3%), there is a possible risk adding more admixture in concrete than calculated. Several researches [5–7] proved that air-entraining admixture dosage is the most significant parameter that affects concrete properties. Using AEAs with overdose may produce a reduction in strength [8], aggravate freeze-thaw damage [9], increase permeability and delay in setting [10]. The aim of this study is to determine the effect of overdose usage of air entraining admixture on concrete properties. For this purpose, it was produced mortars with the use of five different admixture dosages. All components (sand, water, cement) except admixture were treated equally. To determine the fresh state properties of mortar; unit weight, flowability, setting time and air content tests were conducted. To determine the properties of hardened state of mortars; compressive strength, flexural strength and ultrasound velocity were observed. Finally, micro structure analyses were conducted.

2. EXPERIMENTAL STUDY

2.1. Materials

Cement: Locally available CEM I 42.5 R Portland cement, which satisfies EN 197-1, was used. The chemical and physical properties of cement are given in Table 1.

Table 1. Chemical and physical properties of cement.

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
19.42	63.80	4.47	2.70	1.21	0.28	0.59	2.89	4.18

Spec. Gravity	Blaine, cm^2/g	Compressive Strength, MPa		
3.06	3455	25.2 (2-day)	44.9 (7-day)	59.8 (28-day)

Mixing water: As mixing water, Eskisehir tap water was used. The chemical analysis of the drinkable water is given in Table 2.

Table 2. Chemical analysis of mixing water.

pH (20°C)	Cl- mg/l	SO4 mg/l	Mg mg/l	Ca mg/l	Zn mg/l	Cu mg/l	Fe mg/l	NO_3 mg/l	ClO_2 mg/l
7.49	6.53	91.5	41.5	63.8	0.375	0.092	0.074	4.35	< 0.09

Sand: In order to produce mortar, sand that satisfies EN 196-1 was used.

Admixture: In order to investigate the effects of air-entraining admixture, commercially available AEA, supplied from Grace Company, were used and its characteristics are given in Table 3.

Table 3. Properties of AEA.

Properties	AEA
Ingredient	Sodium salt mixture
Color	Brown
State	Liquid
Density g/ml (20°C)	1.009
pH (20°C)	6.6
Total Chloride %	< 0.10
Total Solid (%)	3.6

2.2. Method

In order to observe the differences in concrete by the dosage of admixture, cement and CEN standard sand quantities were set to equal in each mixture. Mixing water was reduced as much as admixture amount. The water-cement ratio is selected as 0.50 for the mortar production. In principle, 5 different norm dosages including control were prepared for each admixture. But in order to reach definitive results for some tests, like compressive strength test, additional dosages in the range of 0% - 2% were applied. The designation and norm dosages of admixtures are given in Table 4.

Prepared mortar was cast into 4 x 4 x 16 cm dimensioned formworks made of steel directly after mixing. The samples were separated into groups, each cured at a constant temperature of 20 °C in the curing pool.

Table 4. The designation and norm dosages of admixture.

Admixture	Optimum Dosage[1]	Dosages and Designations				
AEA	0.06%- 0.2%	0% Control C-0	0.1% AEA-0.1	0.5% AEA-0.5	1.0% AEA-1	2.0% AEA-2

[1]Optimum dosage refers to dosage range that suggested by producer. It refers to a range, because optimum dosage must be assessed after preliminary trials depending upon the actual mix constituents and specifications required.

2.3. Tests

Fresh unit weight was obtained by following EN 12350-6 and using Eq.1.

$$D = \frac{m_2 - m_1}{V} \quad (1)$$

Where D is unit weight (t/m^3), m1 empty weight (t) of cast, m^2 weight (t) of cast with mixture and V is the volume (m^3) of cast.

To evaluate the flowability of mixtures, the flow table tests were carried out following EN 1015-3 [11]. As a test procedure; after lifting the slump cone, two diameters perpendicular to each other are measured and their mean is noted as relative slump.

To measure initial and final setting times, EN 480-2 code was followed. Using Vicat apparatus with the needle of (1.13 ± 0.05) mm diameter, setting times were observed.

Air content in fresh mortar specimens were measured with an apparatus that work with principle of pressure method which is based on Boyle’s law [12]. Prepared mixture was poured into impermeable cast, then cast was pressurized to the certain pressure and then impermeability was removed in controlled manner. At this time air content was observed with the aid of manometer.

Ultrasound wave transmission measurements were implemented using commercially available instrument that satisfies ASTM 597-02. Principally, a pulse is generated at one end of the specimen and the onset of the pulse is picked at the other side. The signal transition duration via specimen is observed. Distance that ultrasound applied to time ratio gives the ultrasound velocity value.

Flexural and compressive strength were measured by means of a hydraulic press. Flexural strength tests were implemented on three 4x4x16 cm dimensioned specimens per mortar, satisfying the EN 1015-11 code. Specimens were placed to 3-point flexural strength apparatus (one-point loading) with the span of 10 mm. The loading rate in flexural tests was 0.05 MPa/sec. The six samples collected from the flexural rupture were used for the compressive analysis. The loading rate in compressive tests was 0.3 MPa/sec. Compressive strength values were collected at ages 7, 28, 56 and 90 days.

After completing mechanical tests on 90 days old specimens, mortar samples were taken, in order to perform microscopic observations. The qualitative phase analysis of hydrated cementitious systems by XRD proved to be a good way of interpreting hydration kinetics [13–15]. In this work, quantitative XRD analysis was carried out to obtain information about the phase compositions of the mortars. For microstructural analysis, diffractograms were recorded with a Panalytical Empyrean diffractometer, operated at 45 kV and 40 mA, from 10 to 80° 2θ at 0.08° increments, using CuKα radiation. All samples were ground to powder, placed to sample holder of diffractogram and measured about 5 minutes. Evaluation of the observed data was performed with the HighScore Plus™ software.

In this work, SEM analyses were carried out using Zeiss Supra 40VP. First, specimens were cut to small dimensions (1 cm x 1 cm) in order to fit into the sample holder. Samples were fixed to sample holder with carbon tape, then samples were covered with platinum using Quorum Q150R ES. Samples were placed to sample room of Supra 40VP and vacuumed environment was provided using inert nitrogen gas. Ensuring the observation conditions, specimens were analyzed and various photos were recorded.

Bruner Emmet Teller (BET) method is a widely used method to obtain porosity of samples, pore size distribution and specific surface area. As a BET analyzer, The Micromeritics Asap 2020 was used for NAD analysis. In the range of 1 to 2.5 g of sample is picked up for NAD analyses. Samples were degassed by pre heating for a designated temperature with a dry, inert nitrogen gas in order to remove moisture in the specimen prior to measurements.

3. RESULTS AND DISCUSSION

3.1. Fresh mortar properties

3.1.1. Fresh unit weight

Because of its nature, air entraining admixtures have an effect of diminishing unit weight of concrete. In this work, it was observed continuous reduction of unit weight with the increasing admixture ratio as seen in Fig. 1. The most important result of this test is that using AEA within the range of optimum dosage, namely 0.1%, has an effect of considerable drop of unit weight which corresponds to 16%, compared to control mixture. Another key point of the graph is that; speed of unit weight drop is diminishing after 0.5% of dosage.

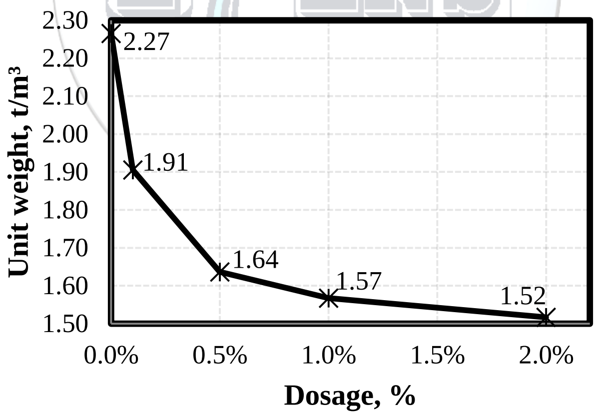


Fig. 1. Fresh unit weight variation depending on admixture dosage.

3.1.2. Flowability (Flow table)

As mentioned in literature, AEAs have an effect of imparting plasticity to the fresh concrete [4,16,17]. As can be seen in Fig. 2, using AEA with the dosage of 0.1%, increased flowability 34% compared to control mixture. But after optimum dosage there is no considerable flowability augmentation, even it can be said that there is no change after the dosage of 1%.

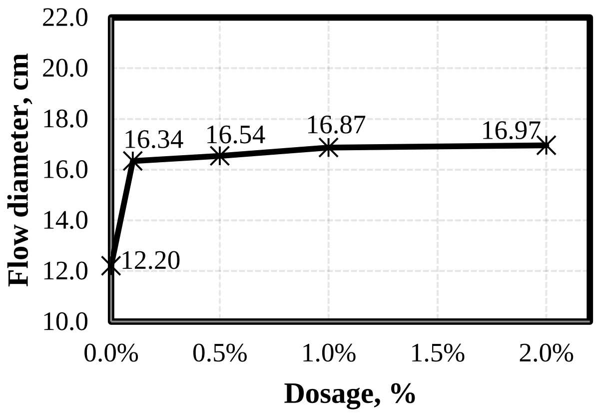


Fig. 2. Flow diameter values obtained from flow table.

3.1.3. Setting times

Fig. 3 illustrates initial and final setting time results. Initial setting times are varying from 179 to 433 minutes, while final setting times vary from 239 to 588 minutes. After certain point for initial setting, namely 0.5%, there is no considerable change for initial setting time while dosage of the admixture is increasing. But, delay of the initial setting time of 2% AEA dosage corresponds to 254 minutes when compared to control mixture. Similar trends were observed for the final setting times. With the increment of dosage, final setting times were extended.

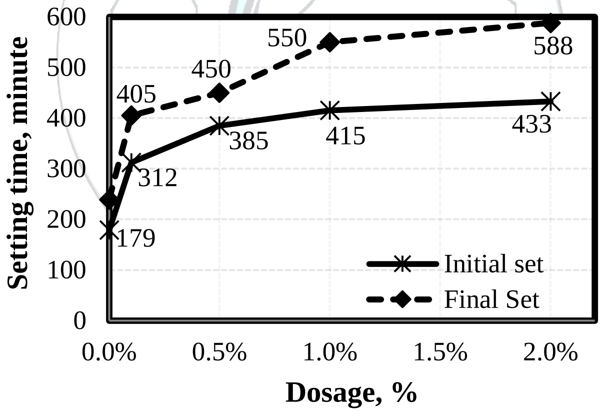


Fig. 3. Initial and final setting time variation depending on admixture dosage.

3.1.4. Air content

Probably the most important parameter for air entrained concrete is air content. As expected, with the increment of dosage, air content in mortar was augmented. As can be seen in Fig. 4, using AEA within the optimum dosage, namely 0.1%, has augmented air content more than twice compared to control mixture. Moreover, slightly exceeding the optimum dosage range, namely 0.5%, air content of mortar specimen escalated to 11.4%, nearly four times of control mixture. But, another significant point of this test is that there is no considerable air content augmentation beyond the dosage of 0.5%. Based on the test results, using AEA more than 0.5% dosage has no avail practically on the base of air content.

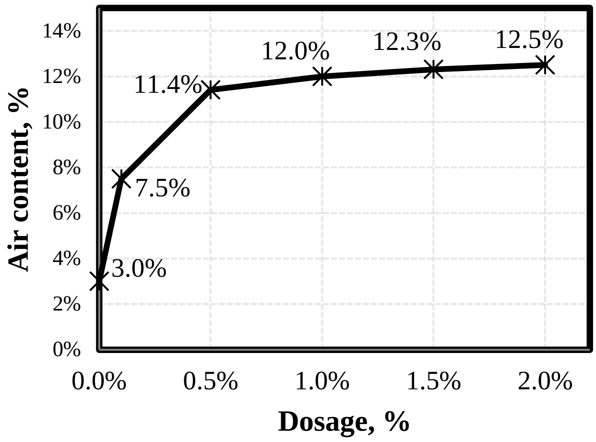


Fig. 4. Air content variation depending on admixture dosage

3.2. Hardened mortar properties

3.2.1. Ultrasound velocity

Ultrasound velocity test results at the age of 28-days are plotted in Fig. 5. Ultrasound velocity values are varying from 2.37 km/sec to 4.09 km/sec for AEA used mortars. AEA used mixtures' ultrasound velocity values were reduced 14.8%, 30.2%, 36.9, %39.6% and %42.7 compared to control mixture at 0.1%, 0.5%, 1%, 1.5% and 2% dosages respectively.

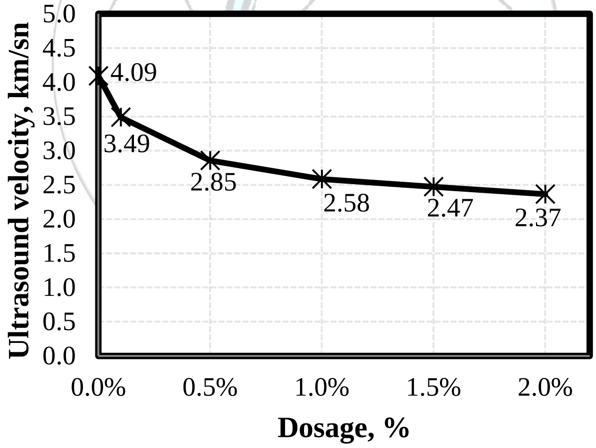


Fig. 5. Ultrasound velocity variation depending on admixture dosage

3.2.2. Flexural strength

AEA used mixtures' flexural strength values at the age of 28-days are presented in Fig. 6. With the augmentation of air content, flexural strength values were diminished because of reverse ratio of air content to strength. AEA used mixtures' flexural strength values were decreased 49.3%, 78.3%, 82.9%, 85.2% and 86.3% compared to control mixture at 0.1%, 0.5%, 1%, 1.5% and 2% dosages respectively. The key point of the graph is that there is a rapid drop of strength up dosage of 0.5%, but beyond this dosage there is no considerable strength drop.

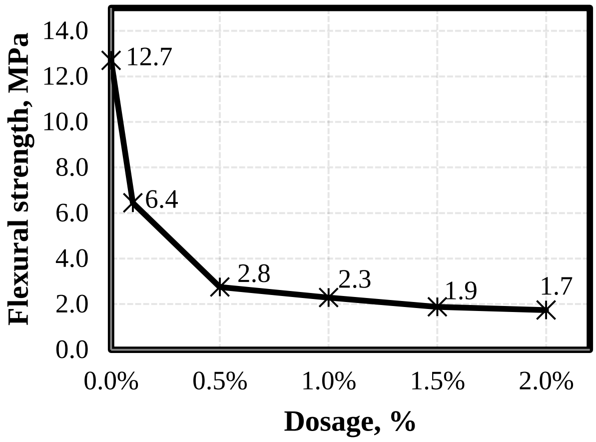


Fig. 6. 28-day aged mortar flexural strength variation depending on admixture dosage.

3.2.3. Compressive strength

Compressive strength tests were conducted at the ages of 7, 28, 56 and 90 days old specimens. Instead of representing each day separately, in order to see strength gain, all values are combined one graph. Fig. 7 illustrates the compressive strength variations depending on time and admixture dosage, for AEA used mixtures. Considering Fig. 7, there is a continuous compressive strength loss with the augmentation of dosage. But on the other hand, speed of compressive strength drop is diminishing after 0.5% of dosage. Although, there is a compressive strength reduction at the dosage of 0.1% compared to control mixture, strength gain depending on time is continuous and stable. But exceeding 0.1%, there is no strength gain depending on time; in other words, specimens reach their ultimate strength nearly at the age of 7 days.

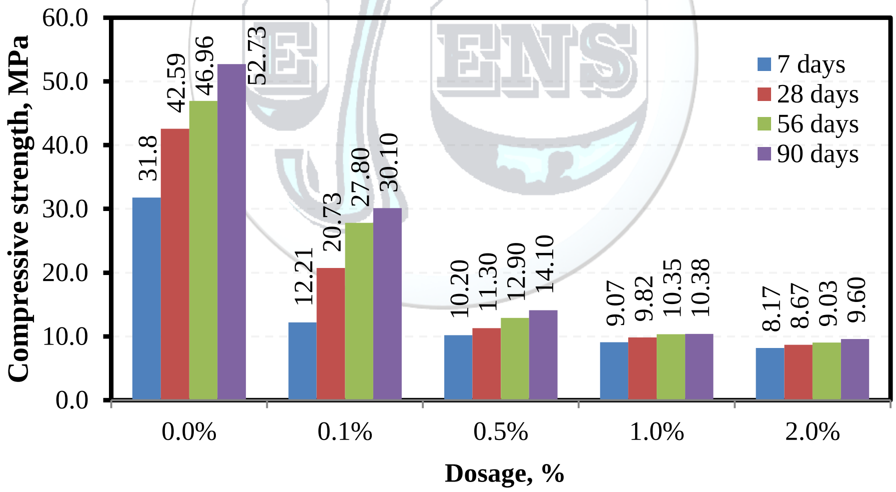


Fig. 7. Mortars compressive strength variation depending on admixture dosage

3.3. Microstructural analysis

3.3.1. X-ray diffraction (XRD) analysis

Because of sand is the main ingredient of concrete proportionally, quarts is the main phase of XRD analysis. XRD analysis of AEA used mixtures for 6 different dosages including control are plotted in Fig. 8. There is no significant phase difference between XRD analysis, because of there is no mineral admixture addition. It can be said that, AEA doesn't change internal structure and/or chemical composition. Physical differences (flowability, strength etc) observed on specimens are due to air content.

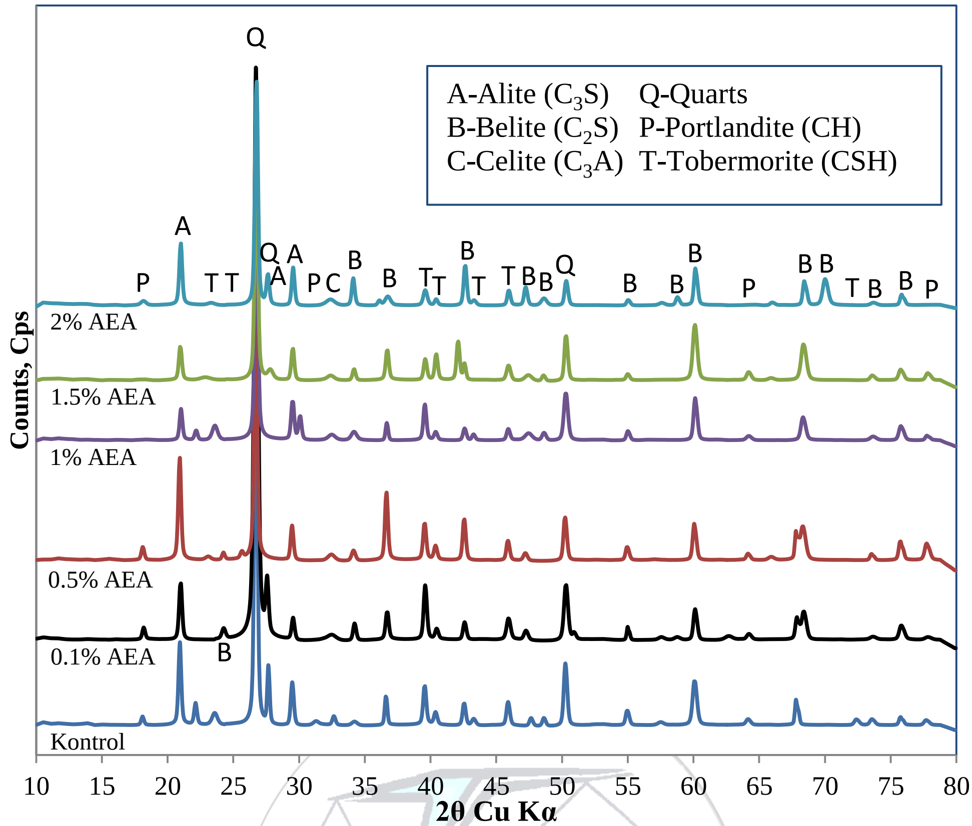
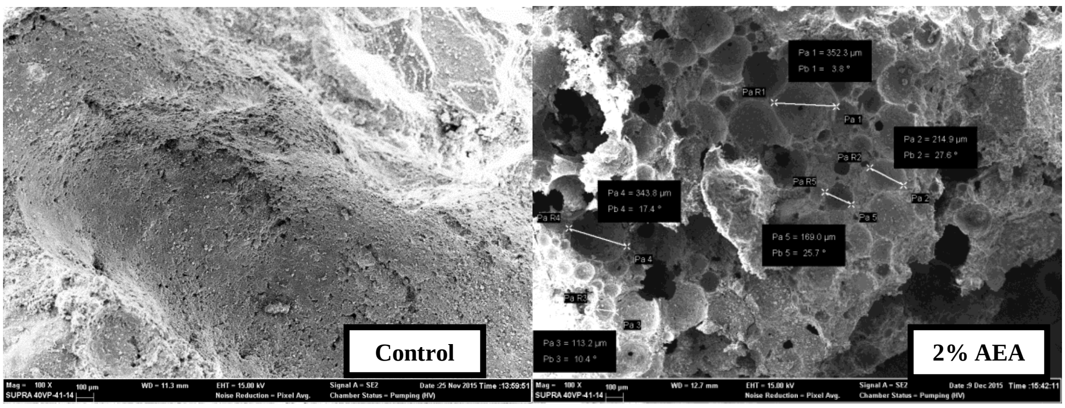


Fig. 8. AEA used mortars XRD analysis.

3.3.2. Scanning electron microscope (SEM) analysis

Fig. 9 shows the result of SEM analysis of the 100 times magnified surface of the AEA included specimens at 90 days-age. Because there is no ingredient in mortar aside from main materials (such as sand, cement and water) that can be seen by SEM analysis, and the basis of the work is the entrained-air, air voids were investigated. Samples used for SEM analysis were taken from specimens with rupture technique, instead of cutting. Since the plane of examination does not usually cut through the center of the spheres [18], in order to observe true air void diameters, rupture technique was applied, because of specimens are tent to rupture the weakest section which is the center of the void. Considering Fig. 9, samples have air voids in the range from 50µm to 500 µm in diameter. It can be easily seen that with the increment of dosage, air void content is augmenting.



(a) (b)

Fig. 9. SEM image of specimens (magnification x100). (a) Without AEA, (b) 2% AEA

3.3.3. Nitrogen absorption/desorption (NAD) analysis

The micropore volume obtained from t-Plot, mesopore volume obtained from Barett, Jonyer and Halenda (BJH) method and total pore, sum of two, are summarized in Table 5.

Table 5. Total pore volume of 90-day aged mixtures.

Type	t-Plot micropore (cm³/g x 10-2)	BJH Desorption mesopore (cm³/g x 10-2)	Total Pore Volume (cm³/g x 10-2)
C-0	0.0436	1.8375	1.8811
AEA-0.1	0.0114	1.4417	1.4531
AEA-2	0.0846	2.0830	2.1676

According to IUPAC (International Union of Pure and Applied Chemistry), sizes of pores are categorized in three groups; macropores (greater than 50 nm), mesopores (between 2 to 50 nm) and micropores (less than 2 nm) [19,20]. With BET analysis, pores less than 500 nm can be analyzed. But, as mentioned before, entrained air voids are in the range of 50 to 300 micron, which equals to 50000 to 300000 nanometer. For this reason, entrained air voids are ignored in BET analysis, because of BET analysis is in nano scale, not in macro scale.

Using AEA within the range of optimum dosage, the total pore amount was less by 22.8% than the total pore amount of the control mixture at the age of 90 days. But, using AEA with overdose, the total pore amount was larger by 15.2% than the total pore amount of the control mixture. According to analysis, using AEA with the dosage of 0.1%, pore volume has decreased. This phenomenon can be explained by workability property. It is known that, air entraining admixtures have an effect of enhancing workability [21], and for this reason pore volume was diminished.

Pore size distribution of three different mixtures is given in Fig. 10. It can be seen that there are two peaks, first one is around 30 Å pore width (left part was unable to measure) and the second one is around 240 pore width. AEA-0.1 mixture has more pores compared to control at first peak, while AEA-2 has the most pores than control and AEA-0.1 at 30 Å pore size. On the other hand, AEA-0.1 mixture has less pores, compared to control at second peak, while AEA-2 again has more pores than control and AEA-0.1 at second peak.

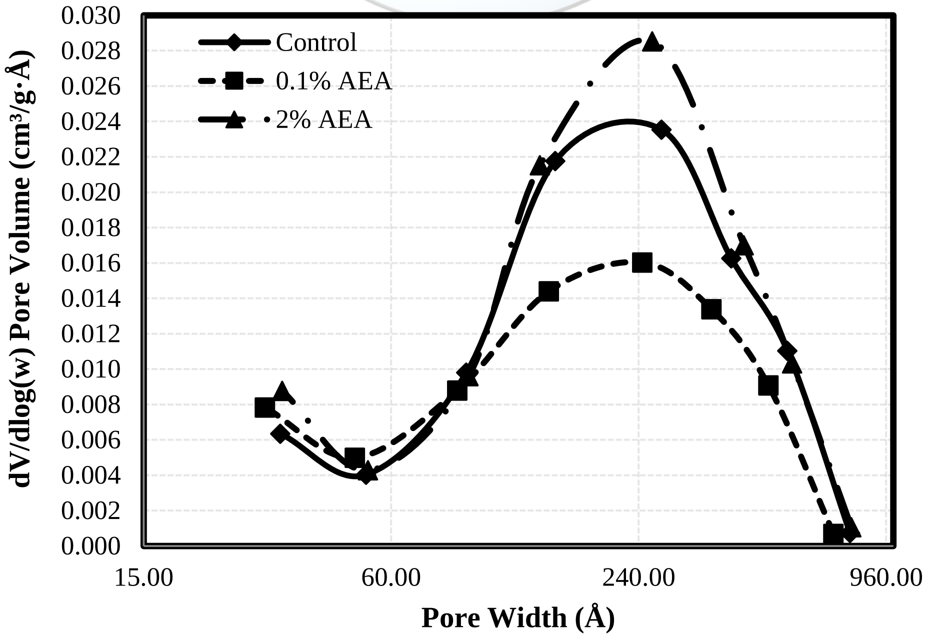


Fig. 10. BJH desorption pore volume curves for three mixes at 90 days.

4. CONCLUSIONS

In this study it was investigated to determine the effect of overdose usage of air entraining admixture on concrete properties. To evaluate the possible effects, fresh state and hardened state tests were conducted. Also as microstructural analyses, XRD, SEM and BET analyses were performed. Based on the experimental results, the following conclusions are drawn:

1. As expected, with the increment of dosage, AEA used mixtures' fresh unit weight values were decreased considerably. This drop corresponds to 33% at the dosage of 2% compared to control mixture.

2. It is known that spherical shape of AEA has an effect of enhancing workability. For this reason, with the increment of dosage, specimens' flowability has augmented. But this augmentation trend tent to slow down after the dosage of 0.1%

3. It can be easily said that AEA usage extends setting times.

4. As expected, the more AEA usage, the more air content in concrete.

5. According to test results, it is obvious that AEA usage decreases the strength of concrete, both flexural and compressive. This result derives from the air void presence. For this reason, AEA must be used carefully on high strength concrete applications.

6. According to micro structural analysis, both XRD and SEM, AEA has no effect on chemical composition and CSH formation of concrete. Differences of the physical properties of concrete with the dosage variation are due to air void presence in concrete.

7. With the aid of BET analysis, it was observed that AEA has a positive effect on diminishing nanoscale pores (less than 500 nm) within the range of optimum dosage. This phenomenon can be explained with workability property. With increasing workability, nanoscale pores are diminishing.

With the sum of all tests and analyses, AEA must be used carefully and within the range of optimum dosages, otherwise there would be loss of physical and mechanical properties of concrete. For this reason, chemical admixtures in general, must be used in process of concrete production in plants and uncontrolled usage in the field must be prohibited.

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