# VALIDATING CONCRETE ADMIXTURE DOSAGES WITH UV-VIS SPECTROSCOPY

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## ABSTRACT

*Admixtures are increasingly used in the field to produce many types of high performance concrete such as self-consolidating concrete. Self-consolidating concrete (SCC) is highly flowable and requires no manual consolidation for placement where there is congested reinforcing steel or where concrete is difficult to place. One of the disadvantages of SCC is its reliance on multiple admixtures to produce the desired effects. UV-Vis spectroscopy was used to investigate the adsorption of the high range water reducing (HRWR) and air-entraining admixtures (AEA), since both admixtures are surface-acting agents when in contact with cement and water. The UV-Vis tests confirmed that the various types of AEA and HRWR behave differently and visually display a difference in the concentration of free admixture in solution. When compared independently and in conjunction with the other, both AEA and HRWR dosages obtained through trial and error could be correlated with the concentration of admixture determined by the UV-Vis Spectrophotometer.*

**Keywords: self-consolidating concrete; admixture; UV-Vis spectroscopy; fresh properties**

## 1. INTRODUCTION

Self-consolidating concrete (SCC) has the ability to flow and consolidate under its own weight, making it well suited for use in areas with heavy reinforcement, complicated formwork, or where mechanical vibration would be difficult. The high fluidity of SCC can cause the mixture to be unstable; therefore, the concrete must also be cohesive enough to fill any shape without segregation or bleeding. The flow ability and viscosity of a SCC mixture are controlled through the use of high range water reducers (HRWR) and viscosity modifying admixtures (VMA), respectively. The HRWR creates the necessary flow ability by adsorbing to cement particles and inducing an electrical charge, thus preventing cement flocs from forming [1]. The VMA increases the viscosity of a mixture by affixing itself to water molecules in the concrete, thus producing a gel-like behavior [2]. An air-entraining admixture (AEA) is also required in order to produce air bubbles dispersed throughout the concrete, which ultimately provides durability for the hardened concrete in freezing and thawing situations.

For self-consolidating concrete mixtures, past research indicates that increasing slump flow increases the demand for AEA to entrain a given volume of air [3,4]. Air bubbles can move about more freely in the concrete when it is highly fluid; therefore, there is increased occurrence of bubble coalescence and rupturing. A SCC mixture with a high viscosity (usually accompanying a lower slump flow) prevents bubbles from rupturing or coalescing by creating a "cushion effect" for air voids to remain unaffected by mixing and other disturbances [5]. While the higher fluidity of SCC can have a destabilizing effect on air voids once they are formed, the usage of admixtures such as VMA and HRWR can reduce the ability of an air-entraining admixture (AEA) to create a proper air void system [4]. The other admixtures can interfere with the ability of AEA to stabilize air voids in the concrete by the way in which they interact on a molecular level.

The main objective of this study was to optimize the dosage requirements using four admixture manufacturers and three slump flows, and validate them using UV-Vis spectroscopy. As such, twelve mixtures were developed in this investigation, utilizing four admixture manufacturers and three slump flows of 559, 635 and 711 mm. An optimized admixture dosage is the minimum admixture dosage required to obtain the target fresh properties (or performance characteristics) outlined below.

## 2. EXPERIMENTAL PROGRAM

### 2.1. Materials

The coarse aggregate used had a nominal maximum size of 16 mm, a specific gravity of 2.79, and was required to pass the #7 gradation limits defined by ASTM C 33 (sieve openings ranging from 12.5 to 4.75 mm). The fine aggregate was also required to meet ASTM C 33 gradation requirements, had a fineness modulus of 3.0, and a specific gravity of 2.78. Fifty-two percent, or 864 kg/m$^3$, of the total aggregate was coarse, and the remaining 48% was fine, or 795 kg/m$^3$. ASTM C 150 Type V cement and ASTM C 618 Class F fly ash were used. All mixture proportions were held constant with the exception of the admixture dosages. The volumetric air content of the fresh concrete was set at 6 ± 0.5%. The water-to-cementitious-materials ratio remained uniform at 0.40. All mixtures contained 390 kg/m$^3$ cement, 78 kg/m$^3$ fly ash, and 187 kg/m$^3$ water (gross). Admixtures were obtained from four different admixture manufacturers available in the United States, and labeled A, B, C and D to prevent endorsement of any manufacturer. The types of each high range water reducing admixture (HRWR), viscosity modifying admixture (VMA), and air-entraining admixture (AEA) utilized from each source can be seen in Table 1.

### 2.2. Mixing and testing program

The concrete was produced in a horizontal pan mixer with 0.0283 $m^3$ capacity. Mixing was done in a consistent manner, with the elapsed time of the total mixing sequence 14 minutes, or 10 minutes following the first cement and water contact. It should be noted that for some admixtures (particularly superplasticizers), the order of addition can have an influence on their performance.

Four fresh properties of the concrete were conducted to assess the flow performance of a SCC mixture: 1) unconfined workability, 2) rate of flow ability, 3) passing ability, and 4) resistance to dynamic segregation. The unconfined workability was tested by measuring the slump flow (described in ASTM C 1611) and was required to be within 13 mm of the target slump flow. The rate of flow ability was determined by measuring the $T_{50}$ (also outlined in ASTM C 1611), which is the elapsed time from when the slump cone is lifted to when the concrete reaches a 50 cm mark on the testing plate. For this study, the $T_{50}$ was required to be between 2 and 5 seconds. The passing ability was determined using the J-Ring, following standard test method ASTM C 1621, and had to be within 51 mm of the slump flow to indicate moderate to high passing ability (refer to ASTM C 1621 blocking assessment). The stability or resistance to dynamic segregation of the concretes was evaluated based on the Visual Stability Index (VSI), as delineated in ASTM C 1611. The VSI, rated on a scale of 0 to 3 (highly stable to highly unstable), was required to be a 0 or 1 (highly stable or stable) for this investigation. The volumetric air content was determined on the fresh concrete in accordance with ASTM C 173. Ultraviolet-visible (UV-Vis) spectroscopy was used to investigate the adsorption of the selected high range water reducing and air-entraining admixtures in cement-water pastes. This instrument measures intensity of the light passing through a sample. The absorbance is a logarithm of the ratio of the intensities of the incident and transmitted lights.

*Table 1. Admixture data*

| | Source | Type | Source | Type |
|---|---|---|---|---|
| (a) High Range Water Reducers (HRWR) | A | polycarboxylate-ester | C | polycarboxylate-acid |
| | B | polycarboxylate-acid | D | polycarboxylate-acid |
| (b) Viscosity Modifying Admixtures (VMA) | A | aqueous solution of polysaccharides | C | dispersed carbohydrate & methyl isothiocyanate |
| | B | naphthalene sulfonate/ welan gum | D | sulfonated naphthalene & melamine polymer |
| (c) Air-Entraining Admixtures (AEA) | A | alkybenzene sulfonic acid | C | saponified rosin and resin acid |
| | B | tall oil and resin | D | natural resin solution |

## 3. DISCUSSION OF RESULTS

### 3.1. Optimum admixture dosages

Trial-and-error procedures were used to achieve the optimum admixture dosages of the SCC mixtures, presented in Table 2. Each mixture is identified using the admixture source (A, B, C or D), followed by the slump flow in mm (i.e. "B-SF559). The overall ranking of sources from the most to the least economical admixture dosage by volume was D, B, C and A. Sources D, B and C tended to have relatively similar HRWR and VMA dosages, whereas source A required a higher amount to achieve the target fresh properties. For all sources the required HRWR and VMA dosages increased with increasing target slump flow. No information on water-to-solid ratio of the selected HRWRs was available.

SCC Mixtures utilizing admixtures from Source A always required VMA in order to create a stable SCC mixture (VSI ≤ 1). The HRWR used from source A had a slightly different chemical composition than the other three sources. Source A consisted of a polycarboxylate-ester (PCE) molecule, as opposed to a polycarboxylate-acid (PCA) molecule. In general, the PCE molecule contains less anionic binding sites to adsorb to the cement particles, but more side chains that allow for better slump retention capability [1]. The PCA molecule has more binding sites which allows for more dispersion of the cement particles, thus imparting greater flow ability to a mixture with a smaller dosage.

*Table 2. Admixture dosages and fresh properties*

| Mixture | Admixture Dosages (ml/kg cementitious materials) | | | Fresh Properties | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | HRWR | VMA | AEA | Slump Flow (mm) | J-Ring (mm) | SF –J-Ring (mm) | $T_{50}$ (sec.) | VSI | Air Content (%) |
| A-SF559 | 2.74 | 0.65 | 0.78 | 552 | 508 | 44 | 2.35 | 0 | 6.00 |
| B-SF559 | 1.50 | 0.00 | 0.33 | 565 | 518 | 48 | 2.53 | 0 | 6.00 |
| C-SF559 | 2.15 | 0.00 | 1.24 | 562 | 498 | 64 | 3.13 | 0 | 6.50 |
| D-SF559 | 1.24 | 0.00 | 0.33 | 572 | 527 | 44 | 2.73 | 0 | 6.00 |
| A-SF635 | 3.39 | 1.24 | 0.78 | 638 | 600 | 38 | 1.93 | 0 | 6.25 |
| B-SF635 | 2.02 | 0.26 | 0.72 | 648 | 610 | 38 | 2.26 | 0 | 6.38 |
| C-SF635 | 2.61 | 0.26 | 1.47 | 640 | 608 | 32 | 2.50 | 0 | 6.25 |
| D-SF635 | 1.83 | 0.26 | 0.59 | 624 | 586 | 38 | 1.92 | 0 | 6.17 |
| A-SF711 | 4.43 | 1.79 | 1.30 | 709 | 671 | 38 | 1.77 | 1 | 6.08 |
| B-SF711 | 2.54 | 0.33 | 0.78 | 715 | 684 | 32 | 2.02 | 1 | 6.00 |
| C-SF711 | 3.00 | 0.33 | 1.37 | 714 | 676 | 38 | 2.25 | 1 | 6.40 |
| D-SF711 | 2.41 | 0.33 | 0.85 | 711 | 699 | 13 | 1.71 | 1 | 6.00 |

The AEA dosages required to entrain 6 ± 0.5% air, as shown in Table 2, did not increase consistently with slump flow for all sources. While increasing fluidity generally increased the required AEA dosage, other factors such as AEA type, and amount of HRWR and VMA present also played a role in determining AEA dosage. Source A was a synthetic detergent AEA, whereas sources B, C and D were wood-derived acid salts. In general, salt-type AEAs react immediately with the ions in cement pastes, creating insoluble water-repellant precipitates that, when caught in the water-air interfaces, tend to remain partially dry [6]. The salt-type AEAs are not generally adsorbed by the cement or other particles within the concrete, but rather the surface tension of water holds the AEA precipitate in the air-water interface. In contrast, synthetic detergent AEAs are pure surfactants that typically form a film at the air-water and air-water-cement interfaces and reduce the surface tension of water [6]. The reduction of surface tension of water prevents the air voids from coalescing into larger air voids through the combined Gibbs-Marangoni effect, thus stabilizing them throughout the fresh concrete [5].

### 3.2. Fresh properties

The actual slump flow, J-Ring passing ability, $T_{50}$ rate of flow ability, VSI, and volumetric air content measured for each mixture design can also be seen in Table 2. The measurements reported are the average of two or three trials for each test, depending on the consistency between trial batches. Time of measurements was kept constant for all trial batches irrespective of the admixture's ability for continued adsorption. The J-Ring test results of the SCC mixtures demonstrated that passing ability increased as the slump flow increased. The $T_{50}$ flow times, which indicate the flow ability and viscosity (by inference) of a SCC mixture, generally decreased with increasing slump flow. The VSI rating determined for each of the twelve mixtures indicated the mixture's dynamic stability, or resistance to bleeding and segregation. A VSI rating of 1 was only given at the largest slump flow of 711 mm for the four admixture sources, which suggests that an increase in slump flow decreases stability. The air content was readily maintained at 6 ± 0.5%.

### 3.3. UV-Vis spectroscopy

In order to validate the differences in optimum admixture dosages between the four sources of high range water reducing admixtures and air-entraining admixtures, ultraviolet-visible (UV-Vis) spectroscopy was conducted on various combinations of admixture-water-cement pastes. Since the exact chemical structure and molecular weight of the admixtures used in this investigation were unknown, research was conducted to compare their behaviors. UV-Vis spectroscopy is useful in explaining the relative trend of optimum admixture dosages, and does not necessarily quantify the amount of admixture adsorbs to the cement particles. The UV-Vis spectroscopy was used to conduct tests of three separate cement pastes with all four admixture sources: a) AEA-cement-water, b) HRWR-cement-water, and c) AEA-HRWR-cement-water.

The procedure for UV-Vis spectroscopy began with first mixing the admixtures with distilled water to create a calibration curve linearly correlating admixture concentration (g/L) with absorbance at a given wavelength. All calibration curves were created at the wavelength of 265 nm, due to its proximity to the peak absorbance value. After establishing the calibration curves for all admixture sources, cement-admixture-water pastes were mixed similarly to the concrete mixtures. The AEA was dosed at a constant 2.0 ml/kg cement, and the HRWR was dosed at a uniform 6.0 ml/kg cement. The admixture dosages were chosen as a mean value typical of all admixture sources, and were kept constant to allow the sources to be compared with each other. Once the admixture-cement-water pastes had been mixed, they were placed in test tubes and centrifuged for 5 minutes at 3500 rpm. Then the liquid was siphoned off the top using a pipette, filtered by 0.20 µm medium, and then tested with the UV-Vis spectrophotometer.

Graphical representation of the UV-Vis spectroscopy on the AEA-cement-water, HRWR-cement-water and AEA-HRWR-cement-water pastes can be seen in Figures 1 (a), 1(b) and 1(c), respectively. For the AEA tests, it can be seen from Fig. 1(a) that sources B, C and D exhibit a hump or peak at approximately 240 nm, whereas source A exhibits a sharp peak at 220 nm and decreases rapidly. From Fig. 1 (b), it can be seen that the HRWR from sources B and D display strikingly similar behavior, while source C has a rounded peak, and source A peaks sharply at a much lower wavelength. The most interesting graph is Fig. 1 (c), where the AEA and HRWR were combined in a cement-water paste. Sources B and D were observed forming large amounts of salt precipitates during testing of the AEA-HRWR-cement-water. The peaks in the combined tests for sources B and D were much wider than the HRWR or AEA alone, indicating a dramatic interaction between the AEA, HRWR and cement materials.

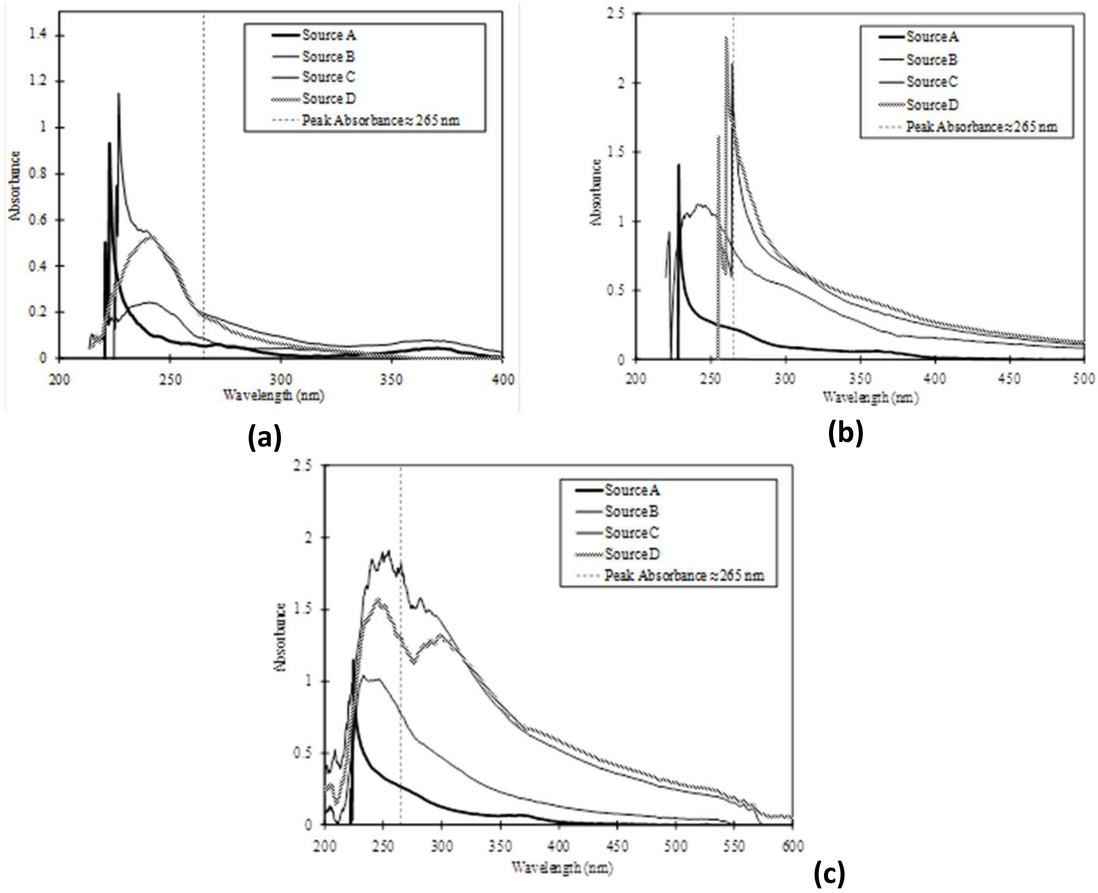


*Figure 1. UV-Vis spectroscopy; (a) AEA-cement-water, (b) HRWR-cement-water, (c) AEA-HRWR-cement-water*

Additionally, tabulated results can be seen in Table 3. For all tests, the effects of cement were subtracted from the curves based on a control batch of cement-water. In

Table 3, in calculating the concentration in solution, the "steady-state" absorbance (assumed to be 700 nm) was also subtracted from the peak absorbance of 265 nm. Then the resulting absorbance value was used in the calibration equation to determine the concentration of free admixture in solution (g/L).

*Table 3. UV-Vis spectroscopy results*

| a) AEA+cement+water | | |
|---|---|---|
| Source | *Absorbance* = A(265) - A(700) | Calculated Concentration, *c* (g/L) |
| A | 0.051 | 0.37 |
| B | 0.186 | 0.36 |
| C | 0.078 | 0.49 |
| D | 0.179 | 0.35 |
| **b) HRWR+cement+water** | | |
| Source | *Absorbance* = A(265) - A(700) | Calculated Concentration, *c* (g/L) |
| A | 0.220 | 15.43 |
| B | 1.701 | 33.96 |
| C | 0.764 | 16.61 |
| D | 1.637 | 194.90 |
| **c) AEA+HRWR+cement+water** | | |
| Source | *Absorbance* = A(265) - A(700) | Calculated Concentration, *c* (g/L) |
| A | 0.271 | 1.86 |
| B | 1.739 | 5.78 |
| C | 0.762 | 13.56 |
| D | 1.229 | 6.85 |

*Table 4. Relationship between UV-Vis data and admixture dosages*

| | | Ranking of Sources | | | |
|---|---|---|---|---|---|
| | | high | → | | low |
| a) | AEA dosage (ml/L)* | C | A | B | D |
| | UV-Vis AEA concentration (g/L) | C | A | B | D |
| b) | HRWR dosage (ml/L)* | A | C | B | D |
| | UV-Vis HRWR concentration (g/L) | D | B | C | A |
| c) | AEA-to-HRWR dosage ratio* | C | D | B | A |
| | UV-Vis AEA + HRWR concentration (g/L) | C | D | B | A |

* Ranking based on average of all 3 slump flows

The calculated concentrations were compared with the required admixture dosages to demonstrate a correlation. For the HRWR-cement-water tests, the highest free admixture concentration (i.e. most admixture available in solution) corresponds to the lowest required dosage, as shown in Table 4. In contrast, for the AEA-cement-water tests, the source with the highest free admixture concentration also had the highest UV-Vis concentration, or the greatest ability to entrain air. For the AEA-HRWR-cement-water test, the highest free admixture concentration corresponds to the greatest AEA-to-HRWR ratio. Therefore, the UV-Vis spectroscopy confirms the optimized admixture dosages established in this investigation.

## 4. CONCLUSIONS

The optimization and testing of admixtures in the production of air-entrained self-consolidating concrete is a time-consuming but necessary process, especially when selecting and using a new product. The results presented in this study demonstrate that admixtures from different sources cannot be used interchangeably, even if they appear to have a similar composition. This study indicated that a polycarboxylate-ester (PCE) HRWR necessitated a larger dosage to impart the same flowability to SCC as a polycarboxylate-acid (PCA) HRWR. Additionally, when using a PCE HRWR, VMA was always required to maintain stability. The SCC mixtures with the most dynamic stability (resistance to segregation and bleeding) were produced with a 559 mm slump flow. UV-Vis spectroscopy was able to validate the trial-and-error approach in optimizing admixture dosages of SCC by indicating the relative trend.

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