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Communication

Paste fluidity of two-component cement dispersant formulation Another additivity rule

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Abstract

Ultrafiltered lignosulfonate (UF-LS), PEO comb-shaped polycarboxylate (PC), and gluconic acid (GA) are formulated with varied ratio, and their dispersion ability is tested in cement paste. While PC and GA formulation follows an ordinary paste flow value additivity (dose–response additivity), UF-LS and PC formulation obeys the additivity in terms of its required dosage for a given paste flow (required dose additivity). The observed required dosage additivity rule may help us further understand cement and multiple-component dispersant interaction.

Keywords: Formulation; Admixture; Cement paste; Dispersion; Workability

1. Introduction

Water-reducing admixtures are widely used in the concrete industry. They allow concrete to achieve the desired workability with less water. Consequently, a water-reducing admixture can give higher strength and durability, or better workability, to concrete. It can also be used to cut cement use at equal performance.

The primary function of the water-reducing admixture is to disperse or deflocculate cement particles, thus giving the cement paste more fluidity. The paste fluidity translates into better workability of concrete [1]. There are numerous publications on the cement dispersing performance of each water-reducing chemical component [2]. However, in practice, the majority of water-reducing admixtures are formulations of several components. The formulation process is the art of the concrete admixture formulator due to its highly complex and proprietary nature. Naturally, there have been few publications on the mechanisms behind this formulation [3].

The present communication presents cement paste fluidity test (minislump) results on three sets of two-component dispersant formulations. The ratio of the two components was varied, and each mixture was applied at several dosages to cement paste. The results are interpreted in terms of "how well they work together." Dispersant chemicals were chosen with high-range water-reduction applications in ready-mix concrete in mind. The chemicals were a comb-type PEO-polycarboxylate (PC), an ultrafiltered lignosulfonate (UF-LS), and gluconic acid (GA). Well-chosen combinations of these chemicals can provide a high level of water reduction coupled with long slump life.

2. Experimental

2.1. Materials

The UF-LS used in the present study was Starflo AD (93.9 wt.% solid powder), the highest grade UF-LS from Georgia-Pacific (Bellingham, WA). The PC was Sokolan HP-80 (35 wt.% aq. solution) kindly provided by BASF (Ludwigshafen, Germany). The GA (technical grade, 50% aq. solution) was a reagent chemical obtained from Fluka (Milwaukee, WI). The ordinary portland cement used was Lafarge Type I/II bagged cement purchased from a local retailer in Western Washington State.

2.2. Formulations tested

Three series of formulations were prepared: Series 1 is the mixtures of UF-LS and PC; Series 2 is the

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Table 1
Solid weight ratio of the components in the formulation series

Series 1: UL-LS/PC formulation (%)						
	1A	1B	1C	1D	1E	1F
UF-LS	0	48.8	69.6	80.0	89.9	100
PC	100	51.2	30.4	20.0	10.1	0
Series 2: PC/GA formulation (%)						
	2A	2B	–	2D	2E	2F
PC	0	50.3	–	80.3	89.8	100
GA	100	49.7	–	19.7	10.2	0
Series 3: UF-LS/GA formulation (%)						
	3A	3B	–	3D	3E	3F
UF-LS	0	50.4	–	80.1	89.9	100
GA	100	49.6	–	19.9	10.1	0

mixtures of PC and GA; and Series 3 is the mixtures of UF-LS and GA. Prescribed amounts of each dispersant solution were mixed to obtain the formulated solutions. Each formulated solution was diluted to a 10-wt.% solution. Table 1 shows the solid weight ratio of the two components in each solution (1A–1F, 2A–2F, and 3A–3F). The admixture dosage in the present experiments was based on the actual total solid weight of the chemicals, and the necessary solution dosage was determined accordingly.

2.3. Cement paste test (minislump)

The minislump test was employed to measure fluidity of cement paste [1]. The method was modified to allow "delayed addition" of the admixture. In the delayed addition mode, a dispersant chemical is added after the cement has been in contact with water (or moisture) for a short time. It is well known that a sulfonic acid-based dispersant, such as lignosulfonate, generally shows much better performance (a lower dosage for the same water-reduction) if a delayed addition procedure is used. As it happened, the PC used also showed a delayed addition benefit with the cement used in this study. The use of delayed addition is important to minimize experimental variation, as well as to reproduce conditions closer to real concrete production. It must also be noted that the fluidity results of the formulations can be vastly different if "regular" addition is employed, (i.e., where the entire admixture is predissolved in all of the mixing water,) and such results can be misleading.

In this work, 300.0 g of cement was first mixed for 1 min in a Hobart mixer with 130.0 g of distilled water. Then, the prescribed amount of admixture was added to paste dissolved in water to a total mass of 20.0 g, and the paste was remixed for another minute. It was then allowed to rest for 3 min, and then remixed again for 2 min. It was then transferred to the standard minislump cone and the spread was measured by recording two diagonal diameters and averaging them. The blank paste data were collected in the same manner except that the

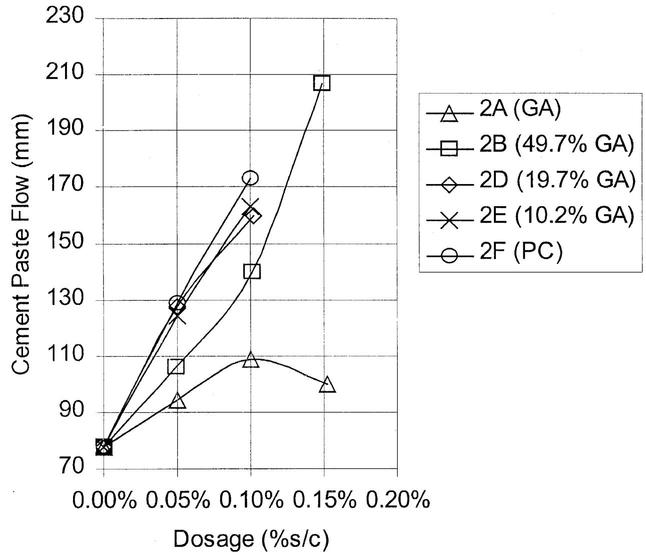

Fig. 2. Dosage–response of the formulation series (2), GA/PC.

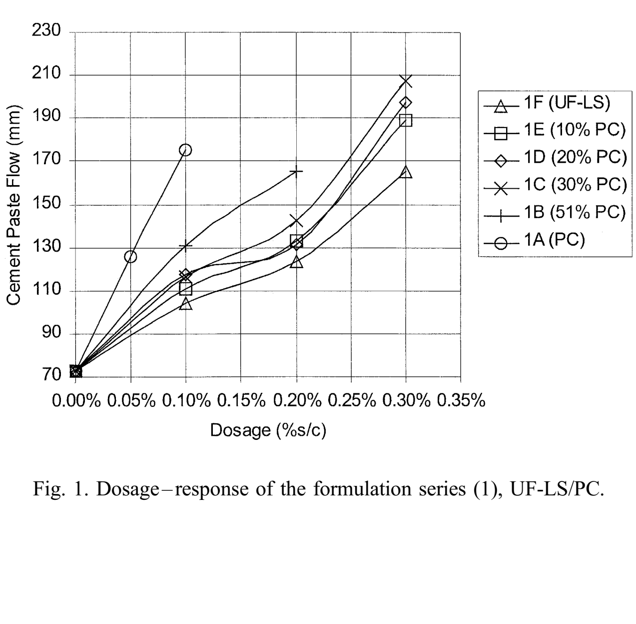

Fig. 1. Dosage–response of the formulation series (1), UF-LS/PC.

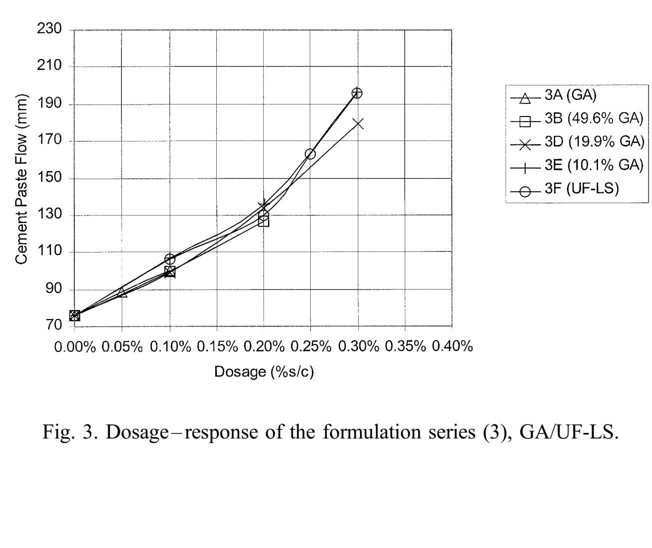

Fig. 3. Dosage–response of the formulation series (3), GA/UF-LS.

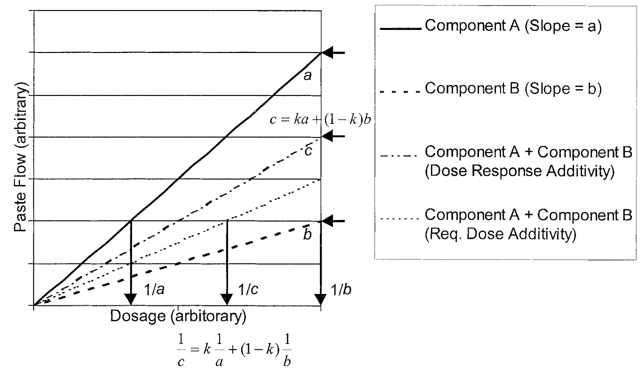

Fig. 4. Representation of two additivity rule models of two-component cement dispersants: dose–response additivity and required dosage additivity.

second addition of 20.0 g of water did not contain any chemicals. It should be noted that even without an admixture, the two separate additions of water gave higher fluidity than adding all of the water at one time. In the present experiment, the amounts of air in all of the paste prepared were insignificant and did not affect the fluidity data.

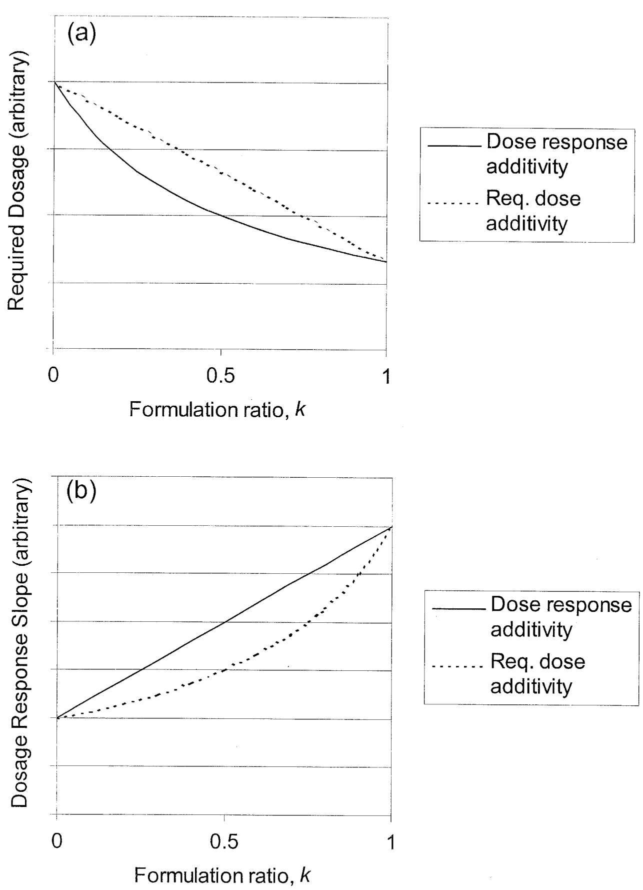

Fig. 5. Required dosage (a) and dosage–response slope (b) curves of the two additivity rule models.

2.4. Data analysis

Minislump data for each formulation were plotted against the applied dosage. In order to eliminate subjectivity, paste flow versus dosage (solid wt.% on cement) data points were fitted by a linear regression using spreadsheet software (MS Excel) to obtain the slope (dosage–response). This first-order fitting was not perfect, but was a reasonable assumption for the purpose. The dosages required to achieve 150 mm paste flow were also estimated from the data. The "slope" data and "required dosage" data were then plotted against the component

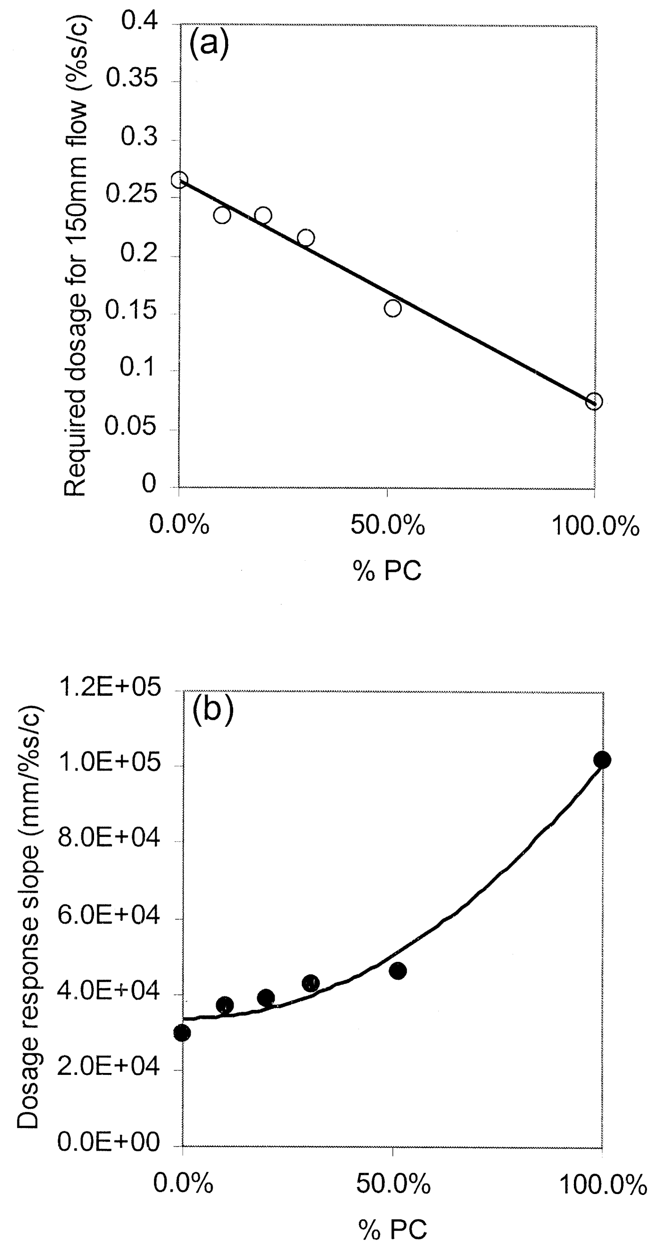

Fig. 6. Required dosage (a) and dosage–response slope (b) curves of the formulation series (1), UF-LS/PC, following required dosage additivity rule.

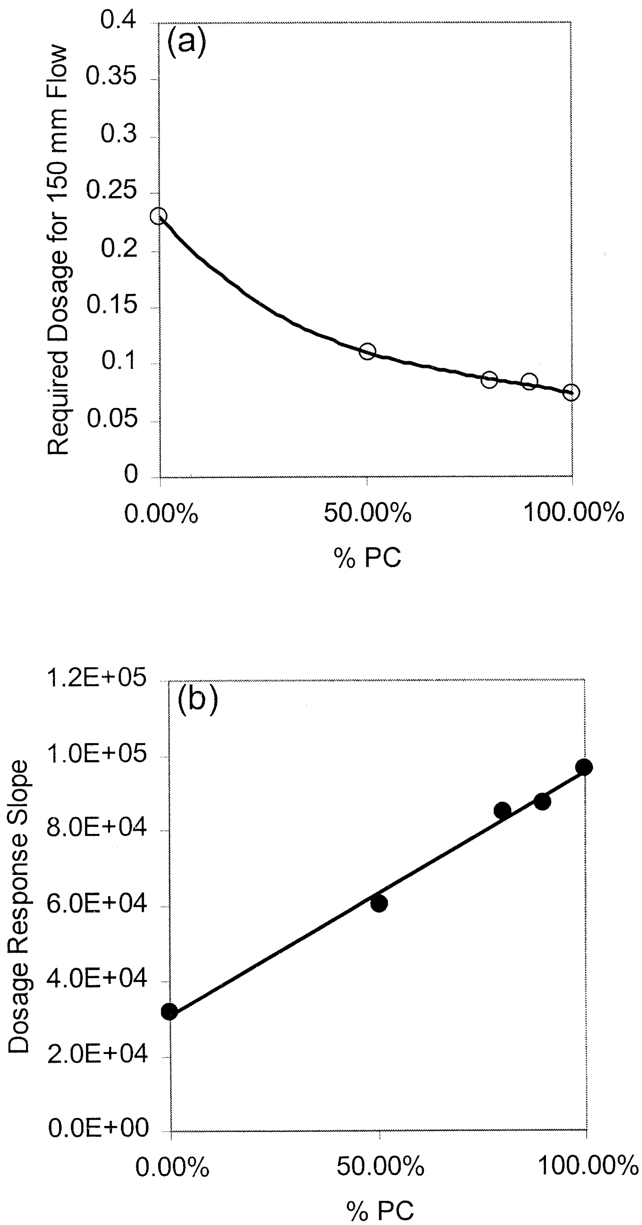

Fig. 7. Required dosage (a) and dosage–response slope (b) curves of the formulation series (2), GA/PC, following response slope additivity rule.

ratios in the formulation to compare with the different additivity models (Figs. 6a,b, 7a,b, and 8a,b).

3. Results and discussion

3.1. Dosage–response results of the formulations with minislump

Figs. 1–3 shows the minislump results of Series 1 (UF-LS/PC), Series 2 (PC/GA), and Series 3 (UF-LS/GA), respectively. UF-LS- and UF-LS-based formulations appear to take-off above the dosage higher than 0.2%, but, in general, a first order linear assumption appears valid for the dosage–response of the admixtures. Paste flow of GA deteriorates above 0.1% dosage. The dosage–response slope and the hypothetical required dosage for 150 mm flow were obtained by extrapolating the 0.05 and 0.1% data points for the sake of model discussion. The dosage–response slope of PC was generally three times larger than that of UF-LS or GA.

3.2. Additivity model

The simplest first order linear relationship between dosage and paste flow was assumed. The slope of the

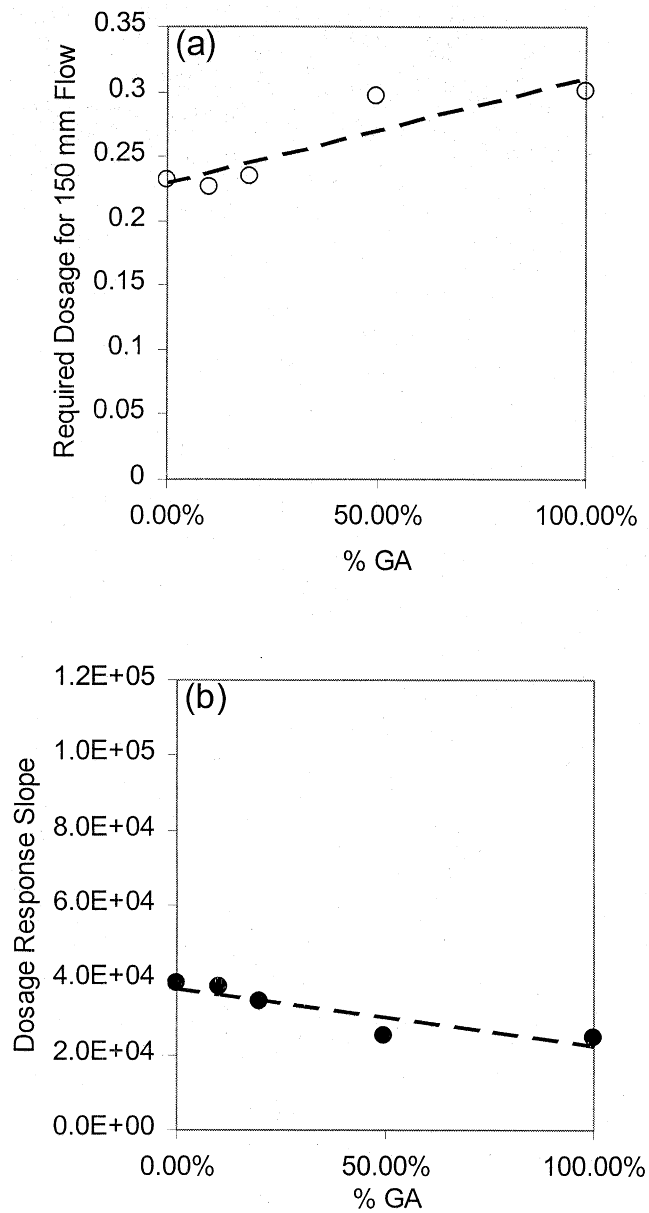

Fig. 8. Required dosage (a) and dosage–response slope (b) curves of the formulation series (3), GA/UF-LS. It is not clear whether this combination shows dosage–response additivity or the required dosage additivity; in either case, the effect is small.

two-component formulation was then calculated according to two different additivity rules, namely, "dosage–response slope additivity" and "required dosage additivity." Fig. 4 shows the dosage–response lines of Component A, Component B, and their formulation with a component ratio of 0.5. With dosage–response slope additivity, the slope of the formulation can be obtained by averaging the slopes of Components A and B in an ordinary arithmetic manner (Eq. (1)), while, with required dosage additivity, the slope of the formulation can be obtained by averaging the slopes in an harmonic manner (Eq. (2)).

$$c = ka + (1-k)b \tag{1}$$

$$\frac{1}{c} = k\frac{1}{a} + (1-k)\frac{1}{b} \tag{2}$$

where a is the response slope of Component A, b is the response slope of Component B, c is the response slope of the formulation, and k ($0 \leq k \leq 1$) is the component ratio in the formulation. (Note that linear slope additivity implies harmonic required dosage additivity, and vice versa.)

Fig. 5a and b, respectively, show the plots of the required dosage for a given flow and the dosage–response slope as a function of the formulation ratio, k, according to Eqs. (1) and (2). By definition, required dosage additivity (Eq. (2)) gives a straight line in Fig. 5a, but gives a concave curve in Fig. 5b, and vice versa for dosage–response additivity [Eq. (1)].

Fig. 6a and b are the required dosage for 150 mm paste flows and the slope the dosage–response of the Series 1 (UF-LS/PC), respectively. The resulting plots indicate that this combination follows the required dosage additivity rule.

Fig. 7a and b are the same plots as Fig. 6a and b, for the Series 2 (PC/GA). Contrary to Series 1, this combination follows the dosage–response slope additivity rule.

Fig. 8a and b are the same plots as Fig. 6a and b, for the Series 3 (UF-LS/GA). Both the required dosages and the slopes of these two components are too close to determine whether the combination follows required dosage additivity or dosage–response slope additivity.

4. Conclusion

It appears there is some confusion in the literature about the so-called "synergistic effects" or "compatibility" as opposed to "destructive interference," or "incompatibility," when more than two water-reducing chemicals are formulated together. The UF-LS/PC formulation appears to show "destructive interference" if we look at the dosage–response slope, whereas it exhibits linear additivity if we look at the required dosage data. Meanwhile, the PC/GA formulation can be considered to have linear additivity by dosage–response, but one may say it has a "synergy" when we look at the formulation's required dosage for a certain slump. The present study suggests that all "synergy" or "destructive interference" observations of formulations of water-reducing chemicals may be reduced to either the slope additivity rule or the required dosage additivity rule. This may not be true for formulations with other, non-water-reducing chemicals.

The above observations appear to have fundamental implications regarding the mechanism. However, much work remains to be done in order to fully understand the origin of the two additivity rules. For example, we must measure each component's adsorption and dispersion behavior with different cement phases. We do not know whether the difference in the additivity is due to the components' adsorption behavior, their dispersion mechanisms after adsorption, or their effects on cement hydration. The author hopes that the present study will provide a new point of view from which to look at water-reducer formulation data, so as to promote new study and help improve our understanding of the action and interference of multicomponent water-reducers.

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