ACI MATERIALS JOURNAL TECHNICAL PAPER

Title no. 101-M50

Effects of Air Entrainment on Rheology

by Leslie J. Struble and Qingye Jiang

The effects of air entrainment on rheological parameters were studied using cement paste. The addition of air-entraining agent increased the air content up to a saturation level, above which no further increase in air content was observed. With increasing air content, the yield stress increased and the plastic viscosity decreased. The increase in yield stress was an unexpected result because increasing air is well known to cause an increase in slump, and yield stress and slump are known to be negatively correlated (as yield stress increases, slump decreases). Two competing effects are proposed to explain the effects of entrained air bubbles on rheological parameters: the attraction of cement particles and bubbles to form bubble bridges, and a fluid response of air bubbles due to their deformability. Bubble bridges are proposed to dominate in the yield stress and the fluid response is proposed to dominate when the sample is flowing.

Keywords: air content; air entrainment; concrete; paste; rheology; viscosity; yield.

INTRODUCTION

Air bubbles in concrete are used to relieve the expansive pressure that develops when water in concrete freezes. Air bubbles are produced by the addition of an air-entraining agent, a chemical admixture that stabilizes bubbles so they persist while the concrete hardens. The typical air-entraining agent provides bubbles in the diameter range 0.1 to 1.0 mm. With bubbles of this size, a typical concrete is protected against freezing-and-thawing damage by the addition of approximately 6% air (throughout this paper the air content is expressed as percent by volume).

Air-entraining agents act by reducing surface tension at the water-air interface. Bubbles are produced by agitation and are stabilized by the air-entraining agent through the reduction in surface tension. Most air-entraining agents are polymeric hydrocarbons that terminate in a polar group, typically carboxylic acid or sulfonic acid, both of which are anionic. Other types are possible, but anionic surfactants appear to be the most efficient.

For several years, our group has been engaged in a research program to characterize the rheology of fresh concrete—the key objective being to enable the use of rheological parameters in formulating concrete mixtures. The principal objective of the present study was to determine the effects of entrained air on rheological parameters of fresh concrete.

Entrained air is known to alter the behavior of fresh concrete by increasing slump. The rule of thumb in concrete mixture proportioning is that slump increases by approximately 10 mm per 1% air (ACI 211.1, "Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete"). At the same time, air is widely recognized to make concrete more cohesive, reducing the tendency of concrete to segregate, whether by bleeding (rising of water to the surface) or settling (movement of aggregate to the bottom). Similarly, air-entrained concrete has been described as sticky, making it somewhat difficult to finish (Edmeades and Hewlett 1999).

Fresh concrete typically shows a plastic (that is, Bingham) flow behavior, a linear relationship between stress and strain rate and a positive intercept on the stress axis. The stress at zero strain rate, determined by extrapolation from positive values of strain rate, is called the yield stress; and the slope of the line is called the plastic viscosity. Parameters that affect the rheological parameters include the amount and grading of the coarse and fine aggregates; the water-cement ratio (*w/c*); the incorporation of mineral admixtures, in particular, those whose particle size distribution is finer than that of the portland cement (that is, silica fume); and the incorporation of chemical admixtures, in particular, those that disperse cement particles (that is, water-reducing admixtures). Although rheological parameters are not routinely measured, slump is a standard measurement on fresh concrete and is widely recognized (for example, Tattersall and Banfill 1983) to be negatively correlated with yield stress (a higher slump corresponds to a lower yield stress) but not correlated with plastic viscosity.

RESEARCH SIGNIFICANCE

This work determined the effects of entrained air on yield stress and plastic viscosity of cement paste and concrete, a necessary step in the development of a rheology-based protocol for concrete mixture proportions. It was known that entrained air increases slump and that slump shows a negative correlation with yield stress, so it was expected that entrained air would act as a fluid, decreasing both yield stress and plastic viscosity. As is shown here, we observed quite different effects, and the explanations provide some understanding of the microstructure of air-entrained concrete.

EXPERIMENTAL PROCEDURES

The tests described here were performed on cement paste. A few concrete samples were prepared to verify the relationship between slump and air content. The materials were a Type I portland cement, three air-entraining agents (herein labeled A,[*] B,[†] and C[‡]), a high-range water-reducing admixture,[§] and ordinary concrete aggregates (the fine aggregate was a siliceous sand and the coarse aggregate was a crushed limestone). All admixtures were obtained as

[*] Alkali-neutralized gum rosin.
[†] Neutralized tall oil.
[‡] A tall oil with α-olefin sufonate.
[§] A sulfonated naphthalene formaldehyde condensate.

ACI Materials Journal, V. 101, No. 6, November-December 2004.
MS No. 03-226 received June 3, 2003, and reviewed under Institute publication policies. Pertinent discussion including authors' closure, if any, will be published in the September-October 2005 *ACI Materials Journal* if the discussion is received by June 1, 2005.

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solutions and the concentration of solid material in each air-entraining agent was determined so the amount of admixture could be expressed on a solids basis. The solids concentration of the air-entraining admixtures was approximately 10% (by mass), and the solids concentration of the high-range water-reducing admixture was approximately 30%.

Most tests were done on cement paste. The pastes used a range of *w/c* levels from 0.40 to 0.55; in addition, tests were made using *w/c* 0.30 in paste containing high-range water-reducing admixture. The dosage of air-entraining agent ranged from approximately 0.05 to 1.0 g solution, 0.0001 to 0.0025 g solid admixture per g cement. Only a single dosage of high-range water-reducing admixture was used, 0.02 g solid admixture per g cement, a dosage we find is needed to provide full dispersion in cement paste.

A typical air-entrained concrete has an air content of approximately 5 to 6% and a paste content of approximately 20 to 40%, so the goal was to achieve air contents up to at least 20% in the paste samples. We found that the standard procedure for mixing cement paste (ASTM C 305, "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency," which uses a paddle mixer) gave air contents only up to approximately 15%, irrespective of the amount of air-entraining agent used. The amount of air depends on the level of agitation during mixing, and it is assumed that more agitation is provided by concrete aggregates than by the paddle mixer, making air contents higher in concrete than in paste. Therefore, a mixing procedure was used that provides more agitation, a commercial household electric mixer.* With this device, we were able to prepare pastes containing air-entraining agents with air contents in excess of 20%.

When mixing paste, we first dissolved the chemical admixtures in the mixing water. Water and cement were mixed by hand for 1 min to avoid loss of mixing water due to splashing, then using the electric mixer for 2 min. Pastes with no air-entraining agent contained approximately 6% air when mixed in this manner. To obtain lower air contents, we vibrated some pastes (on a vibrating table) for a few minutes while applying a modest vacuum. Immediately after mixing or vibration, the pastes were tested for air content and rheological parameters. Pastes were prepared and tested in a laboratory maintained at approximately 23 °C (75 °F), and no special care was taken to control specimen temperature.

To measure the air content of the fresh paste, a 25-mL density bottle, as shown in Fig. 1, was used. First, the mass of bottle filled with alcohol and no paste W_0 and the mass of the empty bottle W_b were determined. Next, the bottle was filled to approximately 20% of its capacity with paste and weighed W_1, then the bottle with paste was filled with alcohol (2-isoproponal) and weighed again W_2. Finally, the bottle was agitated and a mild vacuum applied to remove air bubbles, then filled again with alcohol and weighed W_3. The air content (as percent by volume) of the paste was determined using the following equation

$$A = \frac{W_3 - W_2}{W_0 - W_2 + W_1 - W_b} \times 100 \qquad (1)$$

Replicate samples gave agreement within approximately 1% air. Because of this uncertainty, all values reported herein are the average of duplicate measurements. A few samples were analyzed for air content using a microscopical examination of the hardened paste with linear traverse according to the procedure in ASTM C 457, "Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete." Air contents measured in the hardened paste were consistently lower than air contents measured in the fresh paste by approximately 1.5% air. This difference may simply reflect the increase in solid volume due to cement hydration.

The rheometer used for paste was a wide-gap coaxial cylinder viscometer equipped with a smooth spindle.† The specimen was placed in a 1000 mL cup (approximately 100 mm in diameter) and the spindle (approximately 3 mm

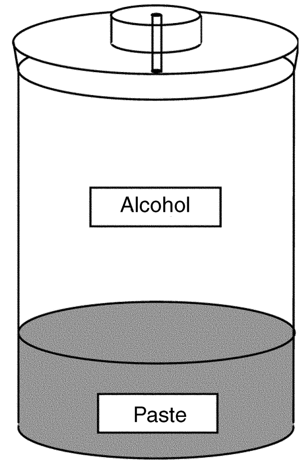

Fig. 1—Density bottle used to measure air content of fresh paste.

Table 1—Concrete proportions

Cement, kg	Water, kg	Fine aggregate, kg	Coarse aggregate, kg
9.70	4.38	15.07	21.36

Table 2—Dosage of air-entraining admixture (AEA) in concretes

Mixture	Dosage (g admixture per kg cement)
1	0
2	1.0
3	2.0

*Five-speed, portable, electric, twin-wheel egg beater, on which only the highest speed was used.

†A wide-gap rheometer, while not desirable, was necessary given the expected large size of the air bubbles. With such a rheometer, the computation of stress and strain is ambiguous. Moreover, such a rheometer may allow slip, which would cause the measured stress to be erroneously low.

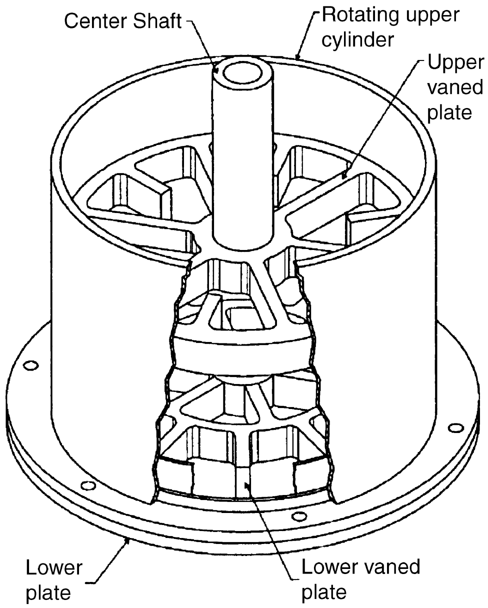

Fig. 2—Concrete rheometer.

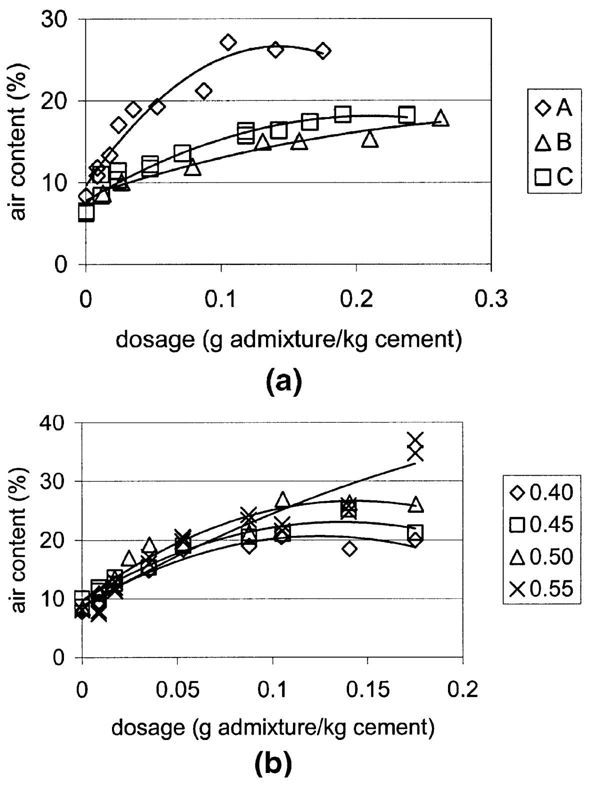

Fig. 3—Air content of paste versus dosage of air-entraining agent: (a) at w/c *0.50 using various air-entraining agents; and (b) at various* w/c *levels using Admixture A (fitted with polynomial functions).*

in diameter) was lowered into the center. Torque was recorded at the following rotational speeds: 60, 30, 12, 6, and 3 rpm. These measurements were started approximately 10 min after mixing first began. This rheometer does not provide simple shear due to its large gap, and values were converted to stress and strain rate using the equations provided by the manufacturer

$$\tau = \frac{T}{2\pi r^2 l} \tag{2}$$

$$\dot{\gamma} = 0.209N \tag{3}$$

where τ is shear stress, T is torque, $\dot{\gamma}$ is strain rate, N is rotation speed (in rpm), r is spindle radius (1.588 mm), and l is spindle length (33.96 mm).

In the concretes, the proportions of materials are given in Table 1, and the dosages of air-entraining agent are given in Table 2. No high-range water-reducing admixture was used in the concretes. The aggregate moisture contents were used to adjust the water contents in the concretes to provide the desired *w/c*; for both coarse and fine aggregate, the absorption capacities were 1.3% and the moisture contents were 0.7%. The concrete tests used only a single *w/c*, 0.45.

Concretes were mixed using a conventional pan mixer. Dry ingredients were mixed for 2 min, water (containing any air-entraining agent) was added, and the concrete was mixed for 4 min. Because the pans on our mixer are slightly concave and some dry material adheres to the bottom and is not mixed, the mixer was stopped after 2 min, the bottom of the pan was scraped by hand, and mixing was continued for the remaining 2 min. Immediately after mixing, the concretes were tested for air content and slump. The air contents for concrete were measured using a standard pressure apparatus following the procedure in ASTM C 231, "Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method," slump was measured following the procedure in ASTM C 143, "Standard Test Method for Slump of Hydraulic-Cement Concrete," and density was measured following the procedure in ASTM C 138, "Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete." The concretes were prepared and tested in a laboratory maintained at approximately 23 °C (75 °F).

The rheometer used for concrete was a pseudo-parallel plate configuration. The design, shown in Fig. 2, is similar to the BTRHEOM rheometer and has been described in detail by Struble, Puri, and Ji (2001). It has a cylindrical container, 240 mm in diameter and 90 mm in depth, with vaned plates at the top and the bottom. The container was filled with fresh concrete approximately 15 min after mixing began (this was the time required to make other measurements). The rheometer was run at 20 revolutions per minute (rpm) for 2 min to provide a homogeneous distribution. Then torque was measured for 10 s at speeds ranging from 20 rpm to 80 rpm. The torque values measured at the same speeds with no concrete were subtracted to correct for friction in the rheometer. Although equations have been established to compute the approximate strain rate and stress from measured values of rotational speed and torque (Struble, Puri, and Ji 2001), they were not used in the present study, rather the results are given as the measured rotational speed and torque values.

RESULTS

Typical paste air contents are shown in Fig. 3. The air contents increased as the dosage of air-entraining agent was increased but leveled off at higher admixture dosages, indicating that there exists a saturation air content for a given *w/c* at a given agitation level. At a given *w/c*, the air content obtained with Admixture A was highest, approximately 25% at *w/c* 0.50 and a dosage of 0.1 g admixture per kg cement, and air contents for Admixtures B and C were lower, approx-

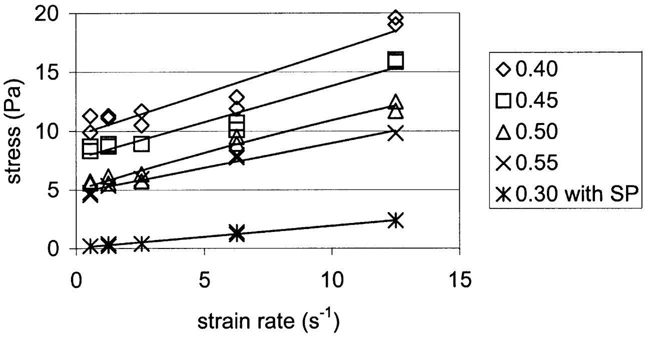

Fig. 4—Flow curves (stress versus strain rate) of pastes at various w/c *levels with no air-entraining admixture, including paste at* w/c *0.30 dispersed with high-range water-reducing admixture (fitted with linear functions).*

imately 15% at the same *w/c* and dosage. At a given dosage of admixture, slightly higher air contents were seen in pastes with higher *w/c* values, indicating that the air content increases with increasing fluidity.

Flow curves for paste with no air-entraining agent are shown in Fig. 4. Similar flow curves were obtained for pastes with air-entraining agents. Results conformed well to plastic behavior, and the fitted lines used to estimate yield stress and plastic viscosity are shown. A slight nonlinearity due to shear thickening was observed in the lower *w/c* pastes. Measurements of cement paste using a more sensitive and more accurate rheometer with a narrow gap between cup and bob have been shown to give flow curves that are better described as pseudoplastic (shear thinning) (Struble et al. 1998). The difference in behavior probably reflects the relative imprecision of the measurements at low strain rates using the wide gap rheometer, but it would not have been possible to use a narrow gap rheometer in pastes containing air bubbles, as the bubbles are too large. The nonlinear behavior confounds the use of linear functions to estimate yield stress and plastic viscosity, and the values computed from the flow curves would obviously be different if some other function (for example, a power function) had been used to fit the rheology data.

It can be seen in Fig. 4 that increasing the *w/c* reduced both yield stress and plastic viscosity. As *w/c* was increased from 0.40 to 0.55, the yield stress decreased from 8.0 to 3.5 Pa and the plastic viscosity decreased from 0.90 to 0.65 Pa.s. Reducing the *w/c* to 0.30 and adding high-range water-reducing admixture at a dosage of 20 g admixture per 1 kg cement reduced the yield stress to zero and reduced the plastic viscosity to 0.19 Pa.s. These behaviors are reasonable and expected.

The effects of air voids on the paste rheological parameters are shown in Fig. 5 and 6. Although there was considerable scatter in the results, it can be seen that yield stress increased linearly and plastic viscosity decreased linearly as the air content was increased. The scatter probably reflects the use of linear functions to fit the rheology data (as in Fig. 4) and the possible occurrence of slip. Scatter may also reflect differences in size and spatial distribution of air voids—parameters that we did not measure. For a *w/c* of 0.40, as air was increased from near zero to approximately 20%, the yield stress increased from 7 to 15 Pa and the plastic viscosity decreased from 1.0 to 0.1 Pa.s. The specific changes in the rheological parameters depended on the *w/c*, but the trends were the same for all *w/c* levels. The slope of the line relating

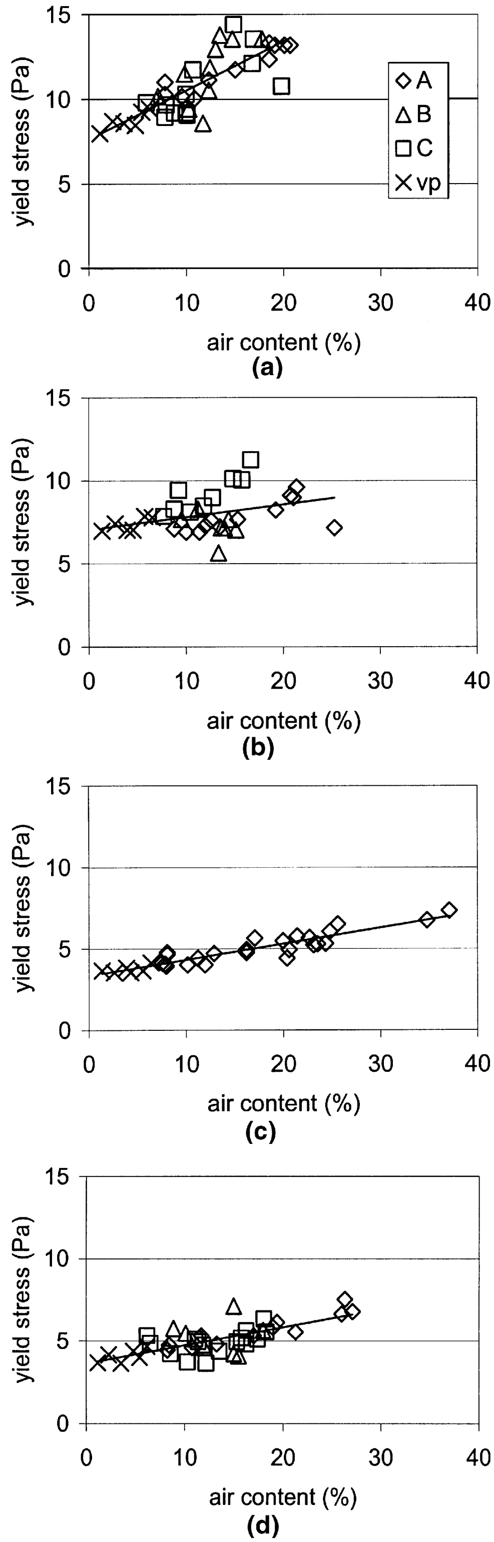

Fig. 5—Yield stress of paste versus air content at: (a) w/c *0.40; (b)* w/c *0.45; (c)* w/c *0.50; and (d)* w/c *0.55 for Admixtures A, B, and C and vacuum-processed (vp) paste (fitted with linear functions).*

yield stress to air content decreased progressively as *w/c* was increased; and the slope of the line relating plastic viscosity to air content increased progressively (became less negative) as the w/*c* was increased. There was no obvious difference in the relationships between yield stress and air content or viscosity and air content for pastes produced using the

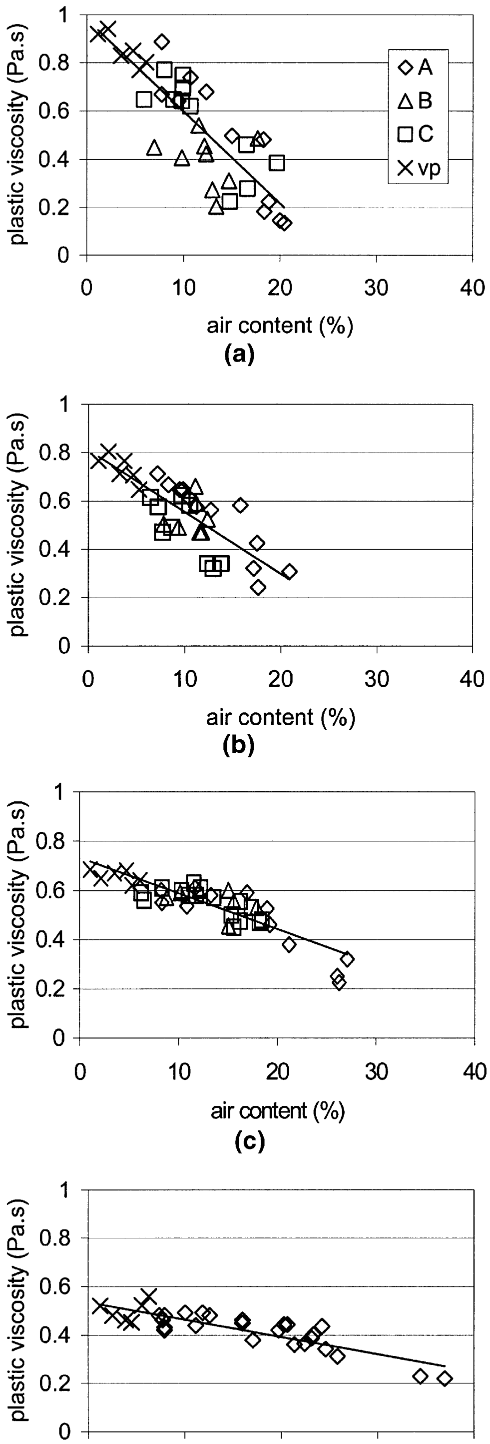

Fig. 6—Plastic viscosity of paste versus air content at: (a) w/c *0.40; (b)* w/c *0.45; (c)* w/c *0.50; and (d)* w/c *0.55 for Admixtures A, B, and C and vacuum-processed (vp) paste (fitted with linear functions).*

different air-entraining agents or for pastes with no air-entraining agent that were subjected to vibration and vacuum to reduce the air content.

Figure 7 shows the effect of the dosage of air-entraining agent (Admixture A) on the air content of paste at *w/c* 0.30 containing high-range water-reducing admixture. The behavior

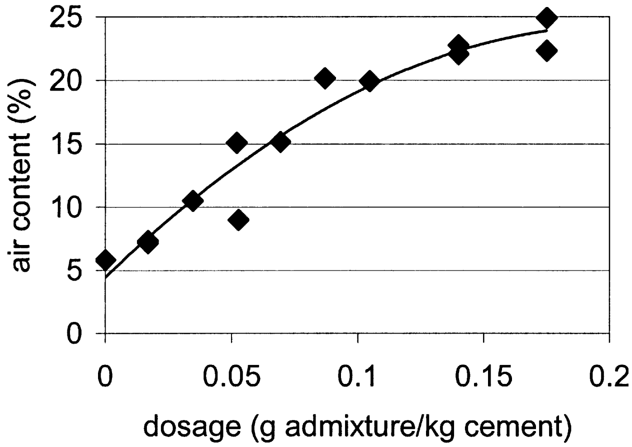

Fig. 7—Air content of paste versus dosage of air-entraining agent at w/c *0.30 using Admixture A dispersed with high-range water-reducing admixture (fitted to polynomial function).*

is similar to that in Fig. 3, except that the maximum air content was quite high, approximately 30%, comparable to the air content in Fig. 3 at *w/c* 0.50. This observation is consistent with our previous observation that higher air contents are obtained in pastes that are more fluid.

Figure 8 and 9 show the effects of air content on the rheological parameters of pastes containing high-range water-reducing admixture. Similar to the results for plain pastes, the pastes dispersed with high-range water-reducing admixture showed an increase in yield stress with increasing air content. But contrary to the results for plain pastes, the pastes dispersed with high-range water-reducing admixture also showed an increase in plastic viscosity with increasing air content.

Measured values of slump, air content, and density are given in Table 3 and flow curves are shown in Fig. 10. The concrete rheology results were consistent with the paste observations, even though the changes in air content were smaller and the rheological measurements were clearly less precise.* The slump increased when entrained air increased, as was expected. The yield stress (proportional to the *y*-intercept in Fig. 10) increased and the plastic viscosity (proportional to the slope in Fig. 10) decreased with addition of air-entraining agent, consistent with our paste results.

DISCUSSION

With no air-entraining agent, the effect of *w/c* on paste flow behavior shown in Fig. 4 is similar to the behavior of other suspensions. When the volume fraction of solids in a suspension increases, both yield stress and plastic viscosity increase. When the particles are dispersed by addition of a high-range water-reducing admixture, the yield stress decreases, but without the high-range water-reducing admixture, the high yield stress indicates a flocculated network of particles that must be broken to initiate flow. It is not so clear that dispersion should also cause a decrease in plastic viscosity, as observed here, but it is clear that dispersion makes the suspension less shear thinning and decreases apparent viscosity at low strain rates, such as used in this study.

*The negative yield stress in Fig. 9 reflects this imprecision. The torque is the difference between the measured value of the empty rheometer and the measured value when the rheometer is filled with concrete. Both are quite large values, so the difference is not very precise.

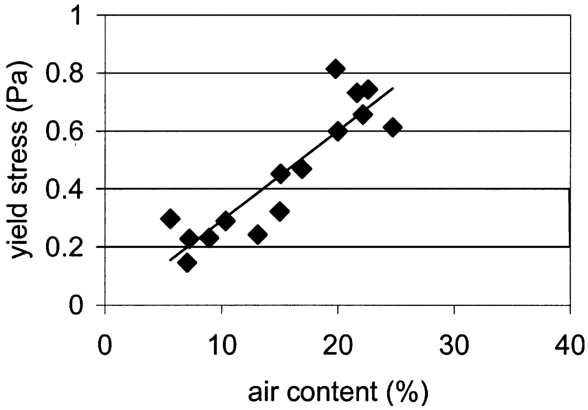

Fig. 8—Yield stress of paste versus air content at w/c *0.30 for Admixture A dispersed with high-range water-reducing admixture (fitted to linear function).*

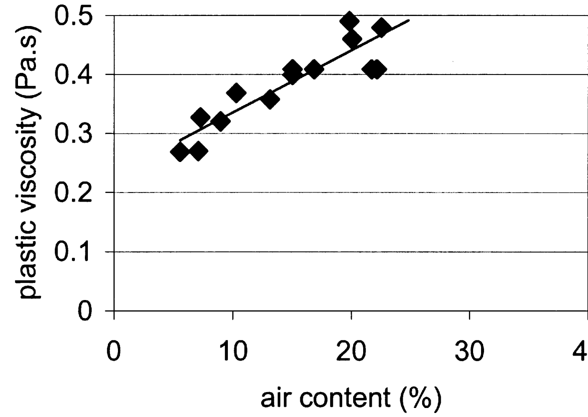

Fig. 9—Plastic viscosity of paste versus air content at w/c *0.30 for Admixture A dispersed with high-range water-reducing admixture (fitted to linear function).*

Figure 5 and 6 show that yield stress increased and plastic viscosity decreased with air entrainment. Rahman and Nehdi (2003) reported similar changes in pastes due to entrained air, the average yield stress increased and the average viscosity decreased by approximately 10% with air. They tested at a single *w/c* and a single dosage of air-entraining agent, however, and did not report the air contents. It should be noted, however, that the changes they reported due to entrained air depended on the rheometer geometry; in fact, the purpose of their study was to assess the effects of geometry and friction on measured properties, and the changes due to entrained air were different in pastes containing fly ash or ground slag.

Figure 5 and 6 show that yield stress and plastic viscosity vary linearly with air content, and it appears from these figures that the slopes and intercepts of these linear functions are related to the *w/c*, so the data were analyzed further to determine the nature of these relationships. Figure 11(a) shows the relationship for yield stress. As *w/c* increased, the slope of the yield stress-air content function decreased; that is, as *w/c* increased, the yield stress became less sensitive to changes in air content. Also, as *w/c* increased, the yield stress at zero air content decreased, which is consistent with the flow curves for pastes with no air-entraining admixture (Fig. 4). Figure 11(b) shows the relationship for plastic viscosity. As *w/c* increased, the slope of the plastic viscosity-air content function became less negative. As already noted for yield stress, as *w/c* increased, the plastic viscosity became less sensitive to changes in air content. This relationship for plastic viscosity was better defined and more nearly linear than the relationship for yield stress. Likewise, as *w/c* increased the plastic viscosity at zero air content decreased, an observation that is also consistent with our flow curves for pastes with no air-entraining admixture (Fig. 4). The increase in *w/c* had a much greater effect on the yield stress than on the viscosity.

The effects of air content on rheological parameters were contrary to our initial expectation. As noted earlier, it is widely agreed that concrete slump increases as air content increases, and it is agreed that concrete slump decreases as yield stress increases. Based on these observations, we had expected that yield stress and plastic viscosity would both decrease as air content increased. This behavior was observed with plastic viscosity, but the effect observed on yield stress was the opposite—yield stress increased as air content increased.

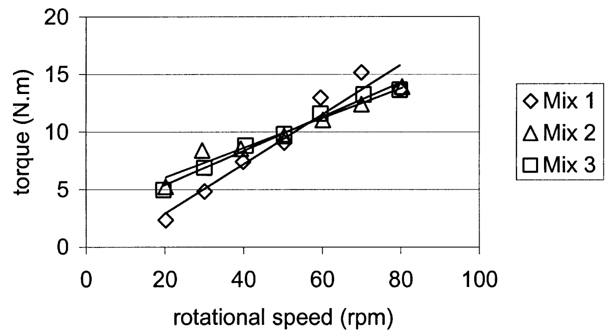

Fig. 10—Flow curves (torque versus rotational speed) of concretes in Table 3.

Table 3—Concrete results

Mixture	Air, %	Slump, mm	Density, kg/m^3
1	1.5	60	2394
2	6.0	70	2307
3	6.5	75	2297

The decrease in plastic viscosity observed when the air content was increased suggests that the air bubbles act as a fluid. Such behavior is not surprising, given that the bubbles are deformable. We therefore analyzed whether the effect of air content on plastic viscosity seen in Fig. 6 is explained by considering the air as an additional fluid. Figure 12 shows the yield stress and viscosity at zero air extrapolated from Figure 5 and 6 versus the calculated volume fraction of solids. Both yield stress and viscosity data were fitted using power functions.* Paste with *w/c* of 0.45 has a volume fraction of 0.41. The addition of 20% (by volume) air reduces the volume fraction to 0.31. Based on the fitted power functions in Fig. 12, the addition of 20% fluid would decrease the yield stress to 2 Pa and decrease the plastic viscosity to 0.3 Pa.s. The

*The Krieger-Dougherty equation is often used to relate apparent viscosity and volume fraction of suspensions. In a previous study, the function was seen to provide good correlation for portland cement pastes dispersed using a high-range water-reducing admixture; this function provided good correlation for nondispersed pastes, although the fitting parameters did not have the same physical significance (Struble and Sun 1995). In this study, however, the authors measured plastic viscosity rather than apparent viscosity and were not able to fit the data in Fig. 11(b) using the Krieger-Dougherty equation. When a power function was fitted to values of apparent viscosity of dispersed paste, it provided good correlation. Furthermore, it nearly superimposed the Krieger-Dougherty throughout the full range of volume fraction.

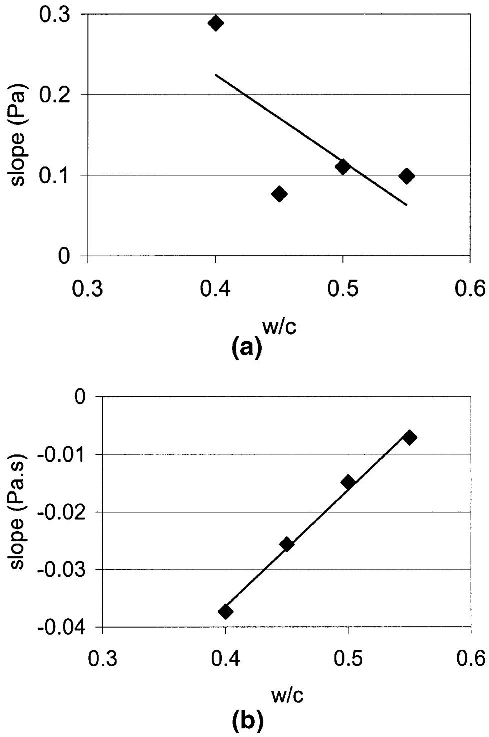

Fig. 11—Slope relating paste rheology to paste air content versus w/c*, showing: (a) slope relating yield stress to air content (from Fig. 5); and (b) slope relating plastic viscosity to air content (from Fig. 6).*

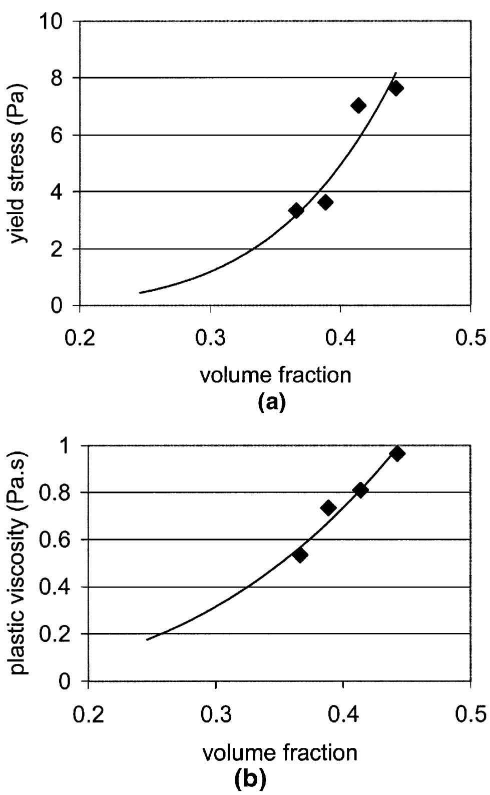

Fig. 12—Rheological parameters of paste versus volume fraction of solids for data at zero air extrapolated from Fig. 4 and 5, showing: (a) yield stress; and (b) plastic viscosity (both fitted to power functions).

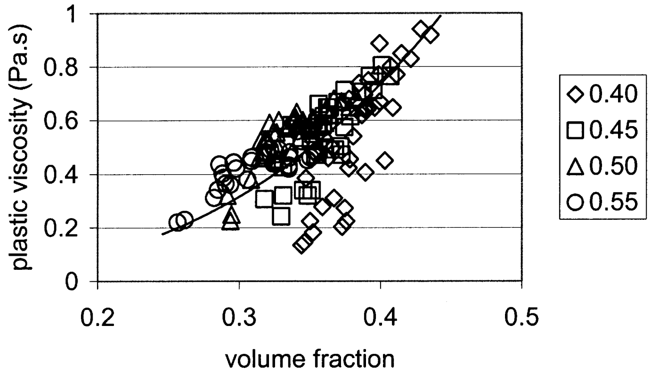

Fig. 13—Plastic viscosity of paste versus volume fraction of solids for all data with power function at zero air from Fig. 12(b).

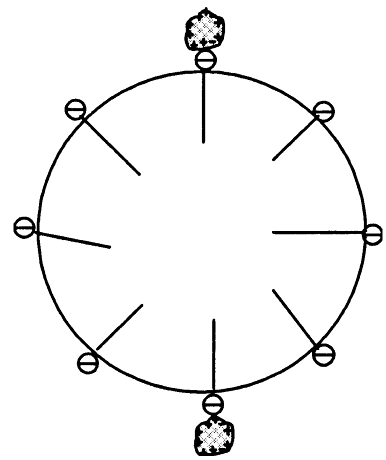

Fig. 14—Schematic diagram of bubble bridging cement particles.

observed effect of adding 20% air was to increase the yield stress to 9 Pa and decrease the plastic viscosity to 0.4 Pa.s. Thus, at least to a first approximation, the effect of entrained air is consistent with air acting as a fluid for plastic viscosity, but not for yield stress. Figure 13 shows the plastic viscosity for all pastes (except those containing high-range water-reducing admixture, which are discussed as follows) versus volume fraction computed with air as a fluid. The pastes results fit the power function in Fig. 12(b) (determined by fitting data for pastes with zero air) quite well, only the *w/c* 0.45 pastes with higher air contents were consistently off the fitted curve. The data in Figure 13 indicate that air bubbles in cement paste reduce the plastic viscosity simply by acting as additional fluid.

One possible explanation for the effect of entrained air on yield stress is provided by a theory proposed by Edmeades and Hewlett (1999) that air bubbles are attracted to cement particles to form bubble bridges. As cement hydrates, the particles become positively charged due to adsorption of calcium ions (Ramachandran and Feldman 1984). With anionic surfactants, air bubbles are negatively charged. Because cement particles are, on average, smaller than the air bubbles, the result is a coating of bubbles by cement particles (Fig. 14), producing bubble bridges between cement particles that increase bonding between particles. These bridges need to be broken for the paste to flow, so they would increase the yield stress. Once the bubble bridges are broken and the paste is able to flow, the air bubbles reduce plastic viscosity, apparently acting as a fluid, as discussed previously. Thus,

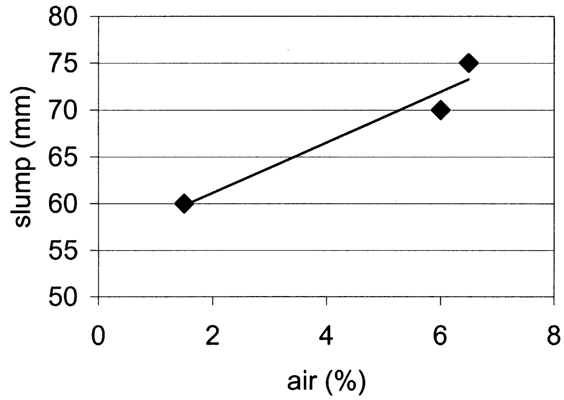

Fig. 15—Slump of concrete versus air content.

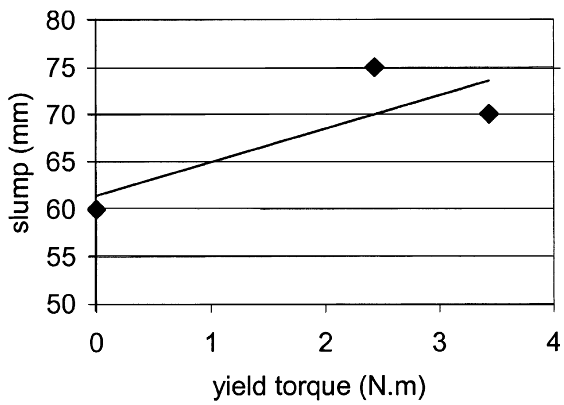

Fig. 16—Slump of concrete versus yield torque.

there is competition between these two actions: without shear, the bubbles act as flocculating particles to increase yield stress; and with shear, the bubbles act as fluid to reduce plastic viscosity.

These effects were modified in our experiments by the addition of high-range water-reducing admixture. In pastes containing both a high-range water-reducing admixture and an air-entraining agent, increasing the air content increased both yield stress and plastic viscosity; whereas in pastes containing only an air-entraining agent, increasing the air content increased yield stress but decreased plastic viscosity. Zeta potential measurements have shown that adsorption of high-range water-reducing admixture produces a more negative surface potential on cement particles and the dispersing action of high-range water-reducing admixtures has been attributed to electrostatic repulsion between negatively charged cement particles (Daimon and Roy 1979; Andersen 1986). If adsorption of high-range water-reducing admixture causes cement particles to be negatively charged, then there would be no attraction between cement particles and air bubbles to produce bubble bridges, and both yield stress and plastic viscosity would decrease with increasing air—not the effect the authors observed. However, the cited zeta potential experiments were carried out in pastes of very low volume fractions (high *w/c*) and consequently do not provide a reliable understanding of the response in pastes with more typical volume fractions. Edmeades and Hewlett (1999) suggested, without evidence, that high-range water-reducing admixtures adsorbed on cement surfaces attract cations from solution to produce a positively charged surface. Air bubbles would then attract such particles to form bubble bridges, as discussed previously. The increase observed in plastic viscosity with increasing air content in the presence of high-range water-reducing admixture suggests that the attraction between cement particles and air bubbles is stronger in the presence of high-range water-reducing admixture; hence, the bubble bridges with high-range water-reducing admixture increase the shear stress even after flow has been initiated.

These results show an increase in yield stress with increasing air content. Such a positive correlation is inconsistent with concrete experience. As noted previously, concrete slump is widely reported to increase with increasing air content and decrease with increasing yield stress. Therefore, the concrete results were examined more carefully. The expected trend between slump and air content, that slump increases as air content increases, was observed (Fig. 15). The expected trend between slump and yield stress, however, was not observed; instead, the slump increased with increasing yield torque (Fig. 16). It appears that air entrainment causes a reversal of the generally reported negative correlation between slump and yield stress. This behavior may indicate that slump occurs not at zero strain rate but rather at some small but finite strain rate. This observation is based on the relatively imprecise concrete rheology measurements but is consistent with the paste measurements, in which one can have greater confidence. The increased yield stress probably accounts for the observed cohesiveness of air-entrained concrete, which is otherwise not consistent with the increased slump. These results provide an example of why slump is a poor indicator of flow behavior and why it is important to measure yield stress and viscosity.

CONCLUSIONS

The following conclusions were drawn from the data and analysis:

1. For a given air-entraining agent, air content increased only up to a saturation level as the admixture dosage was increased. At an admixture dosage above this level, no further increase in air content was observed. The saturation level depended on the sample agitation as well as the particular air-entraining agent;

2. At a given dosage of air-entraining agent, the air content increased with increasing paste fluidity;

3. In pastes with no high-range water-reducing admixture, yield stress increased and viscosity decreased with increasing air content. These effects are explained by two competing actions: the formation of bubble bridges, which increases yield stress, and the fluid action of bubbles, which increases plastic viscosity;

4. In pastes fully dispersed with high-range water-reducing admixture, both yield stress and viscosity increased with increasing air content. It is suggested that in pastes containing high-range water-reducing admixture, the bubble bridges dominate over any fluid action of the entrained air bubbles; and

5. Although a negative correlation is usually reported between slump and yield stress, a positive correlation in air-entrained concretes was observed.

ACKNOWLEDGMENTS

The work described herein was part of the second author's MS thesis. This research was supported by the National Science Foundation through a Young Investigator grant and through the Center for Advanced Cement Based Materials. Both Master Builders Technology (now Degussa) and W.R. Grace provided admixtures. We thank U. Puri and C.-T. Chen for their assistance and discussions, and A. Knell and G. Banas for their experimental assistance.

NOTATION

N = rotational speed, rpm
T = torque, N.m
w/c = water-cement ratio, by mass
$\dot{\gamma}$ = strain rate, s^{-1}
η = viscosity, Pa.s; plastic viscosity is slope in equation $\tau = \tau_0 + \eta_{pl}\dot{\gamma}$ and apparent viscosity is $\tau/\dot{\gamma}$
τ = shear stress, Pa
τ_0 = yield stress, Pa; shear stress at zero strain rate

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