R&D NOTE

Plastic Flow of Saturated Alumina Powder Compacts: Pair Potential and Strain Rate

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Introduction

Yanez et al. (1996) measured the elastic modulus and yield stress of aqueous slurries containing aluminum oxide powder. They produced two different types of attractive particle networks. The network formulated at the isoelectric point (iep = pH 9) was the strongest (Yanez et al., 1996; Leong et al., 1993, Scales et al., 1998), that is, for a given volume fraction, its modulus and yield stress were the largest. At the iep the particles are in contact (that is, in the primary minimum). Weaker networks were formulated by first dispersing the powder (such as at pH 4), and then adding salt (excess counterions). It has been concluded from this (Yanez et al., 1996) and other studies (Velamakanni et al., 1990; Chang et al., 1994) that particles in the weaker network reside in a shallower potential well (the secondary minimum), and thus "sit" apart at an equilibrium separation distance. Rheological data for these slurries strongly suggest that the equilibrium separation distance, and thus, the depth of the potential well, is governed by the surface charge density and the concentration of counterions. In addition, the attractive network formulated by adding salt to an initially dispersed slurry is usually not as strong as the network formulated at the isoelectric point. More recently, it has been shown that the strength of the weaker network is also governed by the particular type of counterion (Colic et al., 1997; Johnson et al., 1999).

It has also been shown that the mechanical properties of a saturated, consolidated powder compact depend on a number of variables that include the interparticle pair potential, the particle packing density, and the consolidation pressure (Franks and Lange, 1996). During pressure consolidation (such as pressure filtration, centrifugation, osmotic consolidation, and evaporative drying), a compressive force is exerted between most adjacent particles. Because the force between each pair of adjacent particles can be very different for different particle pairs (Kuhn et al., 1991), it has been shown that a fraction of the particles can be "pushed" into their primary minimum during pressure consolidation and that this fraction increases with the applied pressure (Franks and Lange, 1996). Since particles that reside in the primary minimum produce a much stronger network relative to those that reside in the secondary minimum, bodies formed above a critical pressure are generally brittle (support crack growth before flow), whereas those consolidated below the critical pressure are generally plastic (flow before fracture).

Even when the body is consolidated below the critical pressure, a small fraction of particles are still pushed into their primary minimum. The strong network produced by this small fraction of particles manifests itself when the body is subjected to stress for the first time (Franks and Lange, 1996). As shown in Figure 1, these plastic bodies initially exhibit elastic loading to a high (peak) stress. When flow initiates, the stress drops to a lower value, called the flow stress. When the body flows, the strong network breaks apart such that the peak stress is never observed during subsequent unloading and reloading cycles, as shown in Figure 1. In addition, the flow stress remains constant during all subsequent loading cycles. The peak stress increases with increasing consolidation pressure, that is, a greater number of particles are pushed into their primary minimum at higher consolidation pressures. When the peak stress is too high, the body fractures before it flows.

In a previous article (Franks and Lange, 1999), we described the effect of particle size and particle morphology on the plastic-to-brittle transition observed in saturated, consolidated alumina powder compacts. In this article, we will describe the effect of the pair potential (as controlled by pH and salt concentration) and strain rate on the plastic flow of the saturated, consolidated alumina bodies formed with one of the powders used in the previous article.

Experimental Procedure

Alpha-alumina powder (AKP-50, Sumitomo Chemical Company, New York, ≈ 0.23 microns average diameter) was prepared as aqueous slurries containing 0.20 volume fraction

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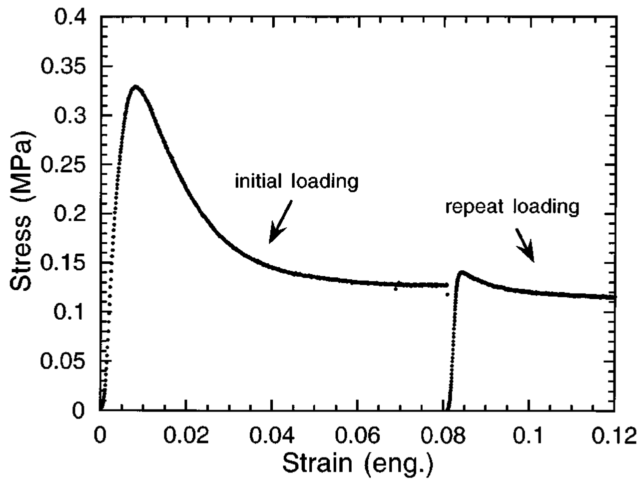

Figure 1. Typical stress–strain for plastic body exhibiting high peak stress on initial loading, but not on subsequent loadings.

The body was consolidated at 5 MPa from slurry formulated at pH 5.0 with 2.0 M NH_4Cl, AKP-50 alumina.

of solids at pH 4.0. After dispersing the aqueous slurry at pH 4.0, it was then either coagulated with additions of NH_4Cl (Fisher Chemical, Fair Lawn, NJ, analytical grade) to create a weakly attractive network, or flocculated to create a strongly attractive network by changing the pH to 9, the isoelectric point of the powder. The pH was adjusted (± 0.1 pH units) with analytical-grade HNO_3 and/or NH_4OH.

The slurries were consolidated by pressure filtration. A predetermined volume of slurry was poured into a pressure filtration cavity, to consolidate cylindrical bodies (1.9 cm dia., height $\approx$ 2.9 cm; aspect ratio $\approx$ 1.5) at 5-MPa pressure. The relative density of the consolidated bodies was determined using the weight-difference method described previously (Franks and Lange, 1999).

Load-displacement measurements were performed using a screw-driven mechanical test machine (Instron model 8562, Canton, MA). The cylindrical bodies (contained within a sealed plastic bag to prevent drying) were loaded in unconstrained, uniaxial compression as described previously (Franks and Lange, 1996). Each experiment consisted of initially deforming the body at moderate displacement rate to reach a constant flow stress beyond the peak stress prior to unloading. The body was then reloaded and unloaded a number of times at various displacement rates with the following schedule: 1 mm/min to ≈ 0.07 strain, then 0.5 mm/min to ≈ 0.14 strain, then 5 mm/min to ≈ 0.21 strain, then 20 mm/min to ≈ 0.28 strain, then 1 mm/min to ≈ 0.35 strain, and finally 1 mm/min to ≈ 0.42 strain. At the end of each loading cycle the machine was stopped to perform a stress-relaxation experiment where the load was measured until it relaxed to a nearly constant value (usually a period of 3 and 8 min). The engineering strain was calculated as the displacement divided by the initial height of the cylinder. To calculate the current area during deformation, the body was assumed to uniformly deform as a right cylinder while conserving its volume. The nominal stress was then calculated by dividing the load by the calculated current area. All stress–strain curves are presented as nominal stress vs. engineering strain.

Results

Flow stresses

Typical stress–strain curves for plastic bodies are shown in Figure 2. Most bodies exhibited an incremental increase in flow stress with increasing displacement rate as shown in Figure 2a. As detailed in Figure 3, some bodies (such as in Figure 2b) exhibited only a slight increase in flow stress with increasing displacement rate. Other bodies, as in Figure 2c, had very large increases in flow stress as the displacement rate was increased. Some of these bodies (as in Figure 2c) did not reach a constant flow stress at the higher displacement rates before the body was unloaded. When a constant flow stress was not observed, the flow stress reported in subsequent graphs was the maximum stress reached before the body was unloaded.

Figure 3 shows the effect of displacement rate on the flow stress of bodies prepared with differing pH and salt concentration. Additional results are presented elsewhere (Franks, 1997). The strength of attraction was controlled by pH and salt concentration. The strongest networks, that is, those with the higher flow stress at a given strain rate, occur when the pH is at or near the isoelectric point of the material (pH 9 for alumina), and when the salt concentration is high. The bodies with the stronger networks (pH 9 and pH 6) have flow stresses that are relatively independent of the displacement rate. The bodies with the weaker networks (pH 4 and pH 5) have flow stresses that increase sharply with increasing displacement rate at rates greater than 1 mm/min.

For displacement rates below 1 mm/min, the flow stress is relatively insensitive to displacement rate. The experiments carried out at the low displacement rates were used to investigate the effect of the strength of the attractive network on the flow stress. Figure 4 shows the flow stresses measured at 0.5 mm/min for bodies formulated at different pH and added salt, that is, with different attractive pair potentials. As expected, bodies consolidated from slurries formulated at pH 6 and pH 9 had higher flow stresses, consistent with a greater particle attraction. Likewise, for slurries formulated to be initially dispersed (pH 4 and pH 5), the flow stress increased with increasing salt concentration.

Stress relaxation

Typical stress-relaxation results for the consolidated alumina bodies are presented in Figure 5a for a body with relatively weak attraction between particles (pH 4.0, 3.0-M salt), and Figure 5b for a body with a stronger attraction between particles (pH 6.0, 1.0-M salt). Figure 6 shows the effect of displacement rate during deformation on the relaxed yield stress of alumina bodies consolidated at 5 MPa, formulated to have varying degrees of attraction. Figure 7 shows how the pH and salt concentration affect the relaxed yield stresses of bodies after testing at 0.5 mm/min, the lowest displacement rate. With the exception of bodies formulated at pH 6, this figure shows that the increase in salt concentration increases the relaxed yield stress. By comparing Figure 5a to 5b, one can see that a greater fraction of the stress is relaxed for

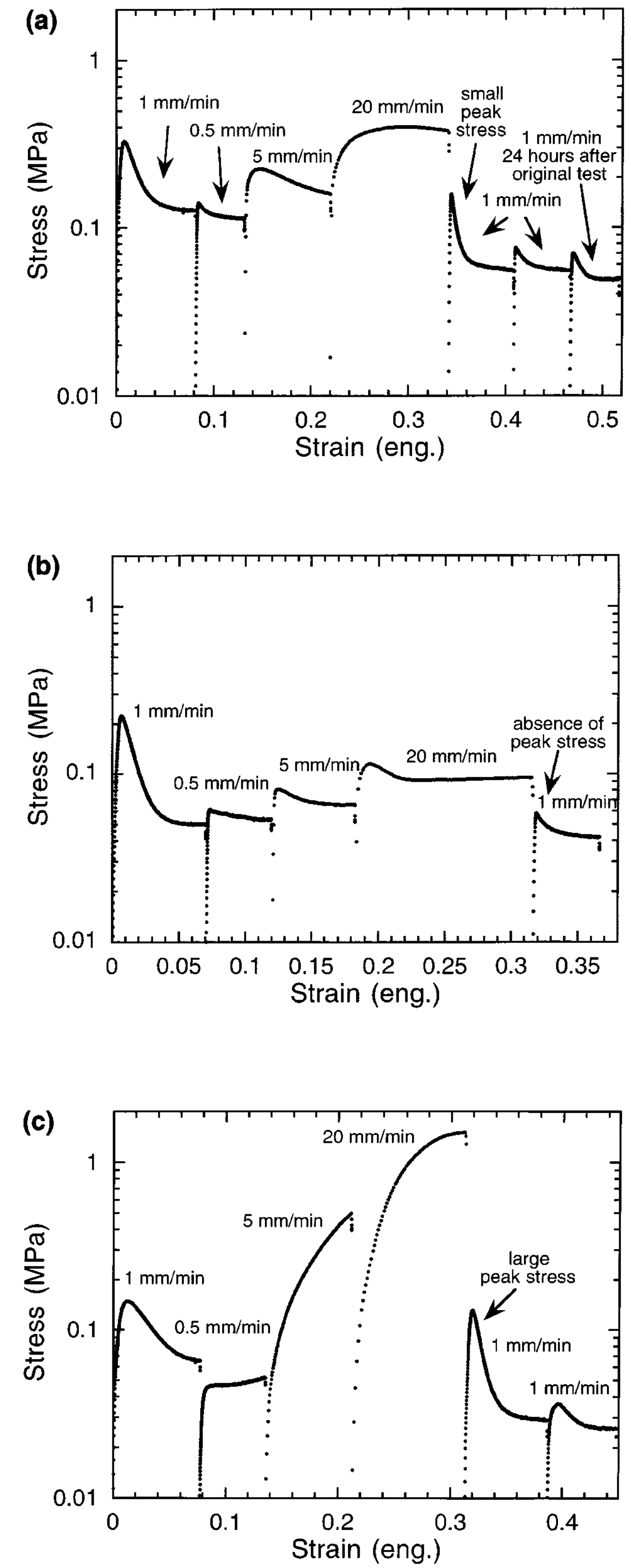

Figure 2. Typical stress–strain for bodies loaded, unloaded, and repeatedly reloaded at various displacement rates.

The bodies were consolidated at 5 MPa and formulated at (a) pH 5.0 with 2.0 M NH_4Cl, AKP-50 alumina; (b) pH 6.0 with 0.5 M NH_4Cl, AKP-15 alumina; and (c) pH 4.0 with 3.0 M NH_4Cl, AKP-50 alumina.

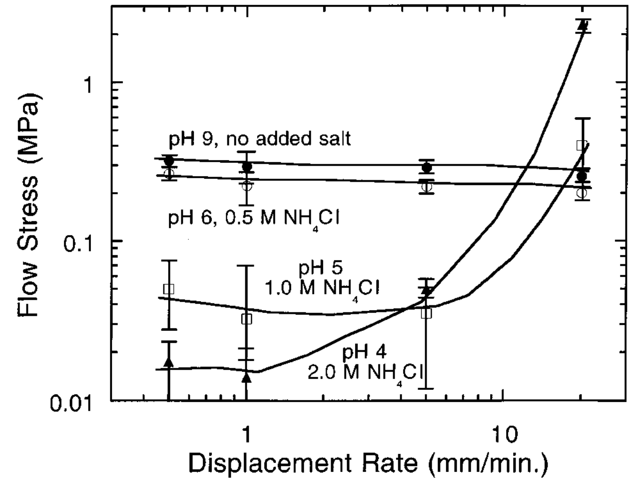

Figure 3. Flow stress as a function of displacement rate for AKP-50 alumina powder compacts with high aspect ratio ($h/d = 1.5$) consolidated at 5 MPa.

The error bars indicate the range of the measurements.

bodies with weakly attractive networks (Figure 5a), relative to bodies with the strongest networks (Figure 5b). Bodies consolidated from slurries formulated to have deep attractive minima do not relax much of their stress, compared to bodies consolidated from slurries formulated with shallower minima.

Discussion

Strength of attraction and flow behavior

Consistent with other data (Yanez et al., 1996; Velamakanni et al., 1990; Chang et al., 1994; Franks and Lange,

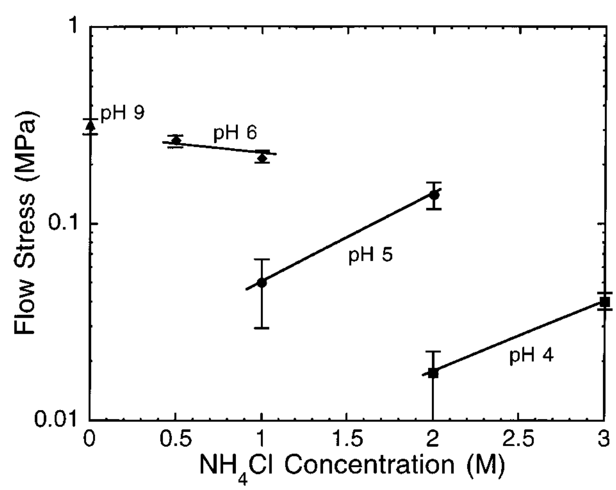

Figure 4. Flow stresses as a function of pH and salt concentration for AKP-50 alumina powder compacts with high aspect ratio ($h/d = 1.5$) consolidated at 5 MPa, and tested at 0.5 mm/min displacement rate.

The error bars indicate the range of the measurements.

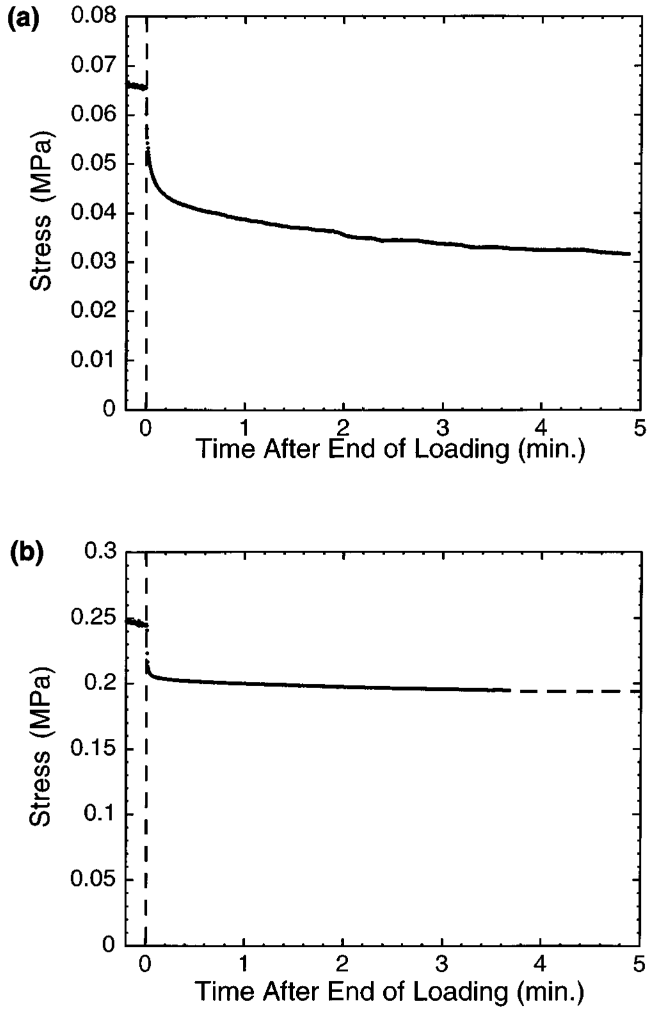

Figure 5. Typical stress relaxation results.

Stress vs. time after the end of the loading cycle for AKP-50 bodies formulated at (a) pH 4.0 with 3.0 M NH_4Cl; and (b) pH 6.0 with 1.0 M NH_4Cl consolidated at 5 MPa and deformed at 1 mm/min.

1996; Leong et al., 1993; Scales et al., 1998; Johnson et al., 1999), the rheological data presented here suggests that the depth of the attractive minimum is controlled by pH and salt concentration. In the absence of any repulsion, the ever-present van der Waals attraction creates interparticle attraction leading to the formation of a strong touching network. Such behavior occurs at the isoelectric point (iep, pH 9 for alumina) where there is no charge on the particles. Changing the pH away from the isoelectric point produces a surface charge, and therefore increases the density of counterions that shroud the particles, creating a repulsive electrical double layer.

The net interparticle potential is the sum of the pervasive van der Waals attractive potential and the repulsive potential produced by the overlapping counterion clouds that shroud each particle. These interparticle potentials (and forces) can be calculated from DLVO theory (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948) to a great degree of accuracy only when the separation distance between the surfaces

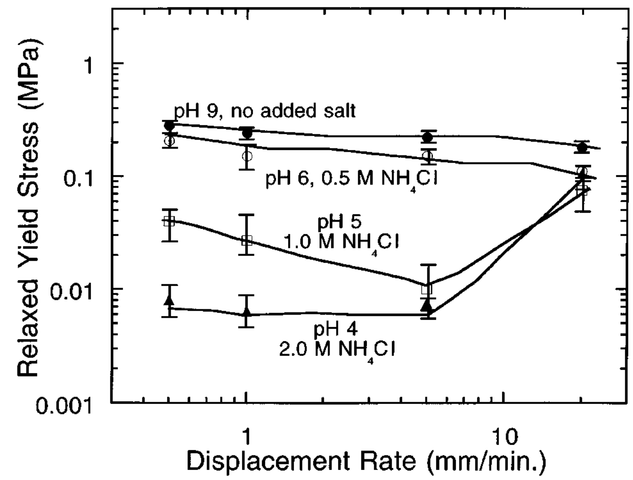

Figure 6. Relaxed yield stress as a function of displacement rate for AKP-50 alumina powder compacts with high aspect ratio ($h/d = 1.5$) consolidated at 5 MPa.

The error bars indicate the range of the measurements.

is large and the salt concentration is low. When the Debye length is large (low salt concentration), the particles are truly repulsive, as a substantial potential barrier will prevent the particles from coming into contact. Increasing the salt concentration decreases the Debye length to create a pair potential with a weakly attractive secondary minimum in which the particles reside.

Unfortunately, the DLVO theory is not applicable for calculating the potential wells for the experimental conditions presented in this work due to the small separation distances and high salt concentrations utilized. There exists no appropriate theory for calculating interparticle forces under these

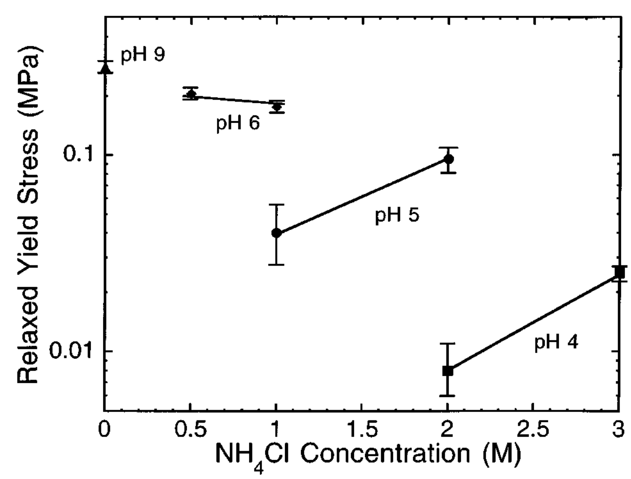

Figure 7. Relaxed yield stresses as a function of pH and salt concentration for AKP-50 alumina powder compacts with high aspect ratio ($h/d = 1.5$) consolidated at 5 MPa, and tested at 0.5 mm/min displacement rate.

The error bars indicate the range of the measurements.

conditions. Thus the flow stress itself must be used as a direct measure of the network strength. Although the exact depths of the minima are unknown, changing the surface charge (by changing pH), would be expected to change the depth of the potential well more significantly than changing the salt concentration within the range of pH's and salt concentrations investigated here.

The results for the flow stress and relaxed yield stress measurements at the two slower displacement rates (0.5 and 1 mm/min, see Figures 3 and 6) are nearly independent of the displacement rate, while at higher displacement rates, this is not always the case. Judging from both the flow stress and the relaxed yield stress at the slower displacement rates (Figures 4 and 7), as well as the previous work (Yanez et al., 1996; Velamakanni et al., 1990; Chang et al., 1994; Franks and Lange, 1996), it can be concluded that bodies formulated at pH 9 and pH 6 have particles that reside in the primary minimum, while those formulated at pH 4 and pH 5 have particles that reside in shallower secondary minima. For the bodies that reside in secondary minima, the strength of attraction increases with increasing salt concentration. That is, the bodies consolidated from slurries at pH 9 and pH 6 had higher flow and relaxed yield stresses. Furthermore, at pH 4 and pH 5 those bodies with a higher salt concentration had higher flow stresses and relaxed yield stresses. In another study (Colic et al., 1997) in which the depth of the attractive minimum was controlled by the type of counterion used to collapse the double layer, the flow stress was found to increase as the depth of the secondary minimum was increased. In addition the relaxed yield stress (after loading at the slower displacement rates) of the bodies formulated at pH 9 and pH 6 is generally greater than that for bodies formulated at pH 4 and pH 5 (see Figure 6). This suggests that it is more difficult for the particles to rearrange when the attraction is strong.

High displacement rates and shear thickening

The flow stress and relaxed yield stress measured for consolidated bodies with deep potential wells (pH 9 and pH 6) are nearly independent of displacement rates. The flow and relaxed yield stresses of the bodies consolidated from slurries formulated to have particles in shallow potential wells (pH 4 and pH 5 plus added salt) tended to increase with displacement rate (see Figures 3 and 6). The increase in flow stress with displacement rate observed for the pH 4 and pH 5 bodies is similar to shear thickening observed in rheological studies of many particulate suspensions (Boersma et al., 1990; Mewis and Spaull, 1976; Metzner, 1985; Barnes, 1989; Keller and Keller, 1990). Many researchers now believe that shear thickening behavior is due to ''particle clustering'' generated by hydrodynamic forces (van Egmond, 1998; and references therein).

By carefully observing the stress–strain results of a body during the loading cycle immediately after it has been rapidly deformed (at 20 mm/min), the presence of a peak stress is noted only for certain bodies. Those bodies that had flow stresses that increased with displacement rate (pH 4 and pH 5) had a peak stress after the fastest deformation rate (compare Figures 2b and 2c). As demonstrated elsewhere (Franks and Lange, 1996), a fraction of the particles can be forced together into their primary minimum during consolidation, resulting in a peak stress, as seen in Figure 1. The observation that a peak stress arises after the body has been subjected to a very fast displacement rate is an indication that a fraction of the particles are ''jammed'' together to form a touching particle network (that is, a volume spanning ''particle cluster''), and are therefore forced into primary minimum contact when they are subjected to the very fast displacement rate. These results strongly suggest that the applied force between particles must increase with the displacement rate applied to the particle network. Such findings are consistent with the increase in force between particles calculated with increasing shear rate due to hydrodynamic interactions, as has been discussed by Boersma et al. (1990). Those bodies formulated at pH 9 and pH 6 do not show a peak stress after the quickest deformation (20 mm/min), since the particles in these bodies already reside in the primary minimum. The conditions necessary for this jamming to occur in saturated, consolidated powder compacts (high density and strain rate) are the same as those that produce shear thickening and dilatant behavior in rheological measurements of colloidal suspensions (van Egmond, 1998; Boersma et al., 1990; Mewis and Spaull, 1976; Metzner, 1985; Barnes, 1989; Keller and Keller, 1990). That is, the same phenomena must be responsible for both behaviors. The high relaxed yield stresses measured for the bodies formulated at pH 4 and pH 5 after being subjected to the fastest loading rate (see Figure 6) suggest that the particles have been pushed together into clusters and thus find it hard to rearrange and relax to lower stress.

Conclusion

Bodies formulated at pH 9 and pH 6 have flow stresses at low displacement rates that were 6 to 10 times greater than the flow stresses of bodies formulated at pH 4 and pH 5 with added salt. This is consistent with the notion that the bodies formulated at or near the iep (pH 9) have particles that reside in the deep primary minimum, while those bodies formulated at pH 4 and pH 5 with added salt have particles that reside in a shallower secondary minimum. The greater attraction of the primary minimum creates stronger bonds between particles that require greater force to cause the particles to rearrange. This means that greater macroscopically applied stresses are needed to produce flow relative to bodies of particles in shallower secondary minima.

The bodies formulated at or near the iep had flow stresses that were nearly independent of the displacement rate. Bodies formulated at lower pH with added salt had flow stresses that increased dramatically with increasing displacement rate. This behavior is similar in many respects to the shear thickening behavior commonly observed in particulate fluids. These bodies appear to have behavior characteristic of bodies that have a strong touching particle network after the body is deformed quickly. This suggests that at least a fraction of the particles are forced together (to form ''particle clusters'') during the fast deformation.

Acknowledgments

The financial support of the Office of Naval Research is gratefully acknowledged. Thanks to Steve Johnson for proofreading the final version of this manuscript.

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Manuscript received June 23, 1998, and revision received Apr. 28, 1999.