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# Shape forming alumina slurries via Colloidal IsoPressing

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## Abstract

The relative density, deformation behavior, and dynamic rheology of bodies consolidated from aqueous alumina slurries, formulated at pH 4 and containing $NH_4Cl$, were studied as a function of the salt concentration (0.1–0.75 M). The smallest salt concentration produced the highest relative density (0.596), which was independent of consolidation pressure. Nearly identical relative densities were obtained for the other salt concentrations, ranging from 0.57 to 0.59 for consolidation pressures of 5–100 MPa, respectively. The consolidated bodies exhibited either a plastic or an elastic behavior when tested in compression. It was observed that the transition from a plastic to an elastic behavior occurred at a critical consolidation pressure. This critical consolidation pressure was directly dependent on the salt concentration. The storage (elastic) modulus for the fluidized, plastic bodies increased with salt concentration. The storage modulus was also observed to be dependent on the time the bodies were allowed to rest after they were subjected to a high shear rate. A pre-consolidated and fluidized slurry formulated to contain 0.5 $NH_4Cl$ was extruded into a rubber mold cavity and further consolidated by isopressing at 200 MPa for 2 min. The body not only increased its relative density (0.58–0.62), but it also became elastic to enable its removal from the rubber cavity without shape distortion. No linear shrinkage was detected after the isopressed bodies were dried. Because of the lack of shrinkage, rapid drying was possible. For example, bar specimens (6.4 mm × 12.7 mm × 60 mm) would survive a 34 °C/min heating rate to 300 °C; the specimen was completely dried within 20 min. Because shrinkage does not occur during drying, bodies could be placed directly into a furnace and heated to 1500 °C for 0.5 h to achieve a relative density of >0.99 and an average grain size of 1.6 μm.

*Keywords:* Powder shaping; Isopressing; Colloidal processing; Rheology; Interparticle pair potential

## 1. Introduction and background

Colloidal IsoPressing is a method for shaping ceramic components with powder suspensions, in a rapid and cost effective manner.[1] This shape forming method was discovered after recognizing that the a strong, short-range repulsive potential exists between particles after salt is added to a dispersed slurry. Fig. 1 schematically illustrates the potential energy between two particles in a dispersed slurry, and the modified interaction after the addition of salt to the dispersion. Prior to the introduction of excessive salt, the interparticle potential is repulsive, and the particles are held apart at relatively large separation distances. With the introduction of sufficient salt, the particles become weakly attractive and 'sit' in a potential well, generally called the secondary minimum. In the well, the particles are separated from one another by an equilibrium distance. When a shear stress is applied to the weakly attractive particle network, the particles can be pulled apart when the force exceeds a maximum value. The maximum force occurs at a separation distance determined by the inflection in the interparticle potential function, at a distance beyond the equilibrium separation. As previously shown,[2–7] increasing amounts of salt will deepen the potential well, and thus raise the maximum force needed to pull the particles apart. Namely, the attractive particle network becomes stronger as the local minimum of the potential well becomes deeper.

Classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DVLO), combines the attractive van de Walls potential with the repulsive potential developed by overlapping clouds of counterions that surround the particles' charged surfaces.[8] The classical theory states that as the counterion concentration is elevated by adding salt, the counterion cloud surrounding particles become compressed, and the range of the repulsive barrier becomes smaller. At sufficiently large concentrations of salt, the classical theory predicts that the repulsive barrier diminishes to zero, leaving only the van de Walls attractive potential. These predictions are not observed in experimental studies, which demonstrated that as more and more salt

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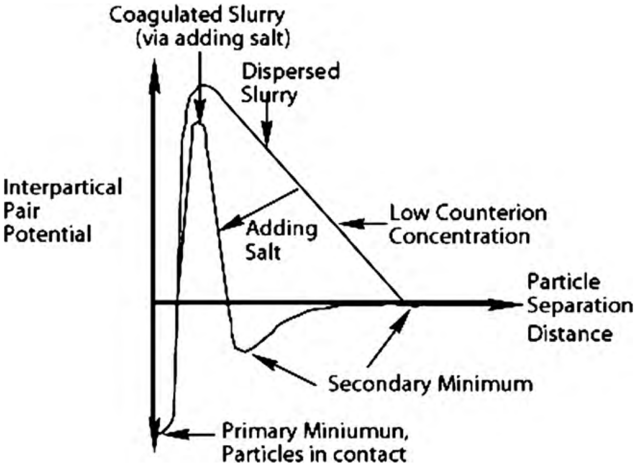

Fig. 1. Potential between two particles as a function of their separation distance. At low concentrations of salt (counterions) the particles are repulsive. Adding salt will produce a deep secondary minimum, where particles are held apart at an equilibrium separation distance.

is added, the secondary minimum become deeper, but a large potential barrier still remains.[2–7] As shown in Fig. 1, the particles become more attractive and harder to pull apart, but, at the same time, the added salt increases the force required to push the particles into contact. This repulsive barrier can become very steep. Since the slope of the barrier is equal to the force required to push the particles together, it can be seen that a much larger force is required to push the particles into contact (into the primary potential well), relative to when the particle are highly repulsive, i.e., the case of the dispersed slurry without added salt. It is this property of the interparticle pair potential that is the basis to the phenomenon of rapid shape forming via Colloidal IsoPressing.

Although the reason for this difference with classical theory is still a matter of conjecture,[9,10] one explanation is based on the principle that the charge between the particles must remain constant as they approach one another.[11] This explanation suggests that the counterions and co-ions surrounding the particles are forced to cancel the surface charges by forming dipoles. The work required to form these dipoles is manifested by the short-range repulsive potential shown in Fig. 1.

The Colloidal IsoPressing method of rapid shape forming takes advantage of the short-range repulsive barrier during the pressure consolidation of a weakly attractive particle network. Franks and Lange[12] discovered that a weakly attractive particle network could be consolidated to dramatically increase the particle packing density, yet, after consolidation, the body could be easily fluidized by vibration. They showed that a critical consolidation pressure exists, below which the consolidated body could be fluidized, while above this critical pressure, the saturated body was elastic and fractured under a compressive stress. Below, it will be shown that the critical consolidation pressure that divides plastic and elastic behaviors depends on the salt concentration in the formulated slurry.

Based on the evidence reported by Franks and Lange[12], Yu and Lange[1] developed the rapid shape forming method, Colloidal IsoPressing. The method starts by formulating a slurry with a highly repulsive interparticle potential In the second step, a predetermined amount of salt is added to produce a weakly attractive particle network. Third, the slurry is concentrated by pressure filtration below the critical stress, where the body can be fluidized by vibration. In the last step, the fluidized body is injected into a rubber mold containing either dry powder or an absorbent material at one end and subjected to a high isostatic pressure. The purpose of the absorbent material is to allow water to be expressed from the saturated body as isostatic pressure is exerted on the powder network. The high pressure pushes the particles over the potential barrier and into contact, as water is expressed into the absorbent material, and the fluid-like body is converted into an elastic body. Once transformed, the component can be removed from the rubber mold without distorting its shape. The recovery strain produced during pressure release is much like that found for cold isostatic pressing: the lower elastic modulus rubber mold recovers more strain than the compressed powder within, thus allowing the body to be easily removed. As shown below, the volume change after isopressing is relatively small, thus, producing a small change in linear dimensions with minimum distortion relative to the rubber cavity. The unique attributes of Colloidal IsoPressing are that complex shaped bodies can be rapidly produced as illustrated in Fig. 2a. In addition, these shaped powder compacts do not shrink during drying, allowing rapid heating to the densification temperature without a pre-drying step.

After it was shown that three-dimensional bodies could be rapidly formed, Zhang and Lange[13] demonstrated that the Colloidal IsoPressing method could rapidly and accurately reproduce complex surface morphologies. They used an elastomeric PDMS (poly(dimethylsiloxane)) mold to form an inverse replica of the surface of the coin shown in Fig. 2b. During this investigation, it was found that if the spacing between deep surface features was too small, the isopressed powder compact would fracture during unmolding. To solve this problem, Zhang and Lange[14] found that they could strengthen the saturated, isopressed body by a gelation method pioneered by Morissete and Lewis.[15] This gelation procedure was tailored such that the two agents used did not affect the rheology of the pre-consolidated slurry, but only caused gelation during the isopressing step. It was shown that the addition of the gelling agents could increase the strength of bar specimens by a factor of 3. This strengthening enabled the replication of surface features as small as 5 μm, and periodic linear channels of this dimension with an aspect ratio of 2:1.

The purpose of the current work is to illustrate the effect of salt concentration on the properties of the pre-consolidated slurries prior to the isopressing step. These properties include the consolidation pressure that defines the plastic to elastic transition, the particle packing density achieved during pre-consolidation, and the rheological properties of the pre-consolidated bodies. In addition, it is demonstrated that the bodies formed by Colloidal IsoPressing can be placed in a furnace, without a pre-drying step, and heated to their densification temperature.

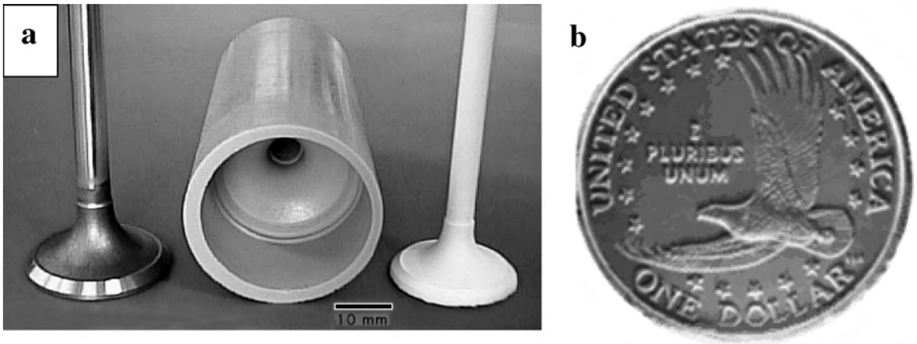

Fig. 2. (a) Forming a ceramic value (powder compact) using a PDMS rubber mold of a metal value via Colloidal IsoPressing.[1] (b) Coin molded with PDMS and formed into a alumina powder compact via Colloidal IsoPressing.[13]

## 2. Experimental

### 2.1. Pre-consolidation and rheology studies

Aqueous slurries containing 0.20 volume fraction of α-alumina powder (Sumitomo Chemical Co., Grade AKP-50, 0.25 μm diameter) slurries were prepared with deionized water. The slurries were dispersed at pH 4 using $HNO_3$. Prior to the addition of any salt, the slurries where rolled in plastic bottles, then the pH was adjusted to the desired level with either $HNO_3$ or $NH_4OH$. A series of coagulated slurries were formulated by adding different amounts (0.1–0.75 mol/L) of $NH_4Cl$. This increase in electrolyte concentration would transform the dispersed particles into a weakly attractive particle network. All slurries were equilibrated in a sealed plastic bottle and agitated for a minimum of 24 h.

In separate experiments, the slurries were consolidated by pressure filtration[16] at pressures between 2 MPa and 100 MPa. Two different cylindrical, stainless steel dies were used for pressure filtration: a 25 mm diameter die used for creating specimens for uniaxial compression tests, and a 45 mm diameter die for rheological experiments after the consolidated compacts were fluidized. After a low-pressure period that allowed a compact to form on the filter (Whatman Inc., Grade 50), the pressure was elevated and fixed at the desired pressure (Fred S. Carver Inc., Carver Laboratory Press). The pressure was held until the plunger ceased to move for at least 15 min.

The relative density of the saturated, consolidated bodies was determined by a weight loss method. First, the consolidated specimen was weighed while still saturated with water. The change in weight after drying for at least 24 h at 70 °C determines the mass of water loss from the saturated compact. The dry specimen was then heated to 500 °C for 3 h to vaporize the salt left in the consolidated body. The final mass (assuming only alumina remains) and the change in weight after drying and heating can be converted to volumes of alumina, water, and ammonium chloride respectively, using the associated densities (3.98 g/cc, 1.0 g/cc, and 1.5 g/cc respectively). The volume of alumina divided by the total volume (alumina, water and salt) resulted in the relative density of the consolidated alumina compact.

Consolidated bodies not used for density measurements were immediately transferred to a plastic bag containing a piece of damp paper towel to minimize evaporative loss of water prior to and during mechanical testing.[12] The bag was sealed and each specimen was tested within 20 min from the time it was removed from the die cavity. Uniaxial compression tests were performed on the consolidated bodies with a displacement controlled mechanical testing machine (Instron Co., Model 8562). Typical specimen dimensions were 25 mm in diameter and ~25 mm in height. The cross-head displacement rate was set at 1 mm/min. All plastic specimens were compressed to ~20% of their initial height. The engineering stress and strain were calculated from the measured load and displacement based on the initial specimen dimensions. The peak stress recorded for each specimen was defined as the maximum stress that the specimen was able to support prior to an abrupt drop in load due to either flow or fracture.[12]

Dynamic rheology experiments were performed with bodies that were consolidated at 5 MPa and could flow, after vibration, to fill the measurement cup for the rheometer. A stress controlled rheometer (Rheometrics Inc., Model DSR) with a vane and cup geometry (vane diameter: 16.0 mm, length: 31.0 mm; cup diameter: 32.0 mm) was used. The vane tool has been successfully used to measure the properties of concentrated slurries that would otherwise cause a slip at the wall with a Couette tool, a common problem for high volume fraction slurries.[4,17] Any touching particle network that may have formed during consolidation was broken apart with the aid of vibration (Cleveland Vibrator Company, CM-30). The liquefied compact was extruded and vibrated into the rheometer cup. After insertion of the vane tool, a thin layer of mineral oil was floated over the entire slurry surface to minimize water evaporation during the experiment.[4] A dynamic stress sweep test (DSST) was immediately performed to determine the yield stress, using a fixed frequency of 1.0 rad/s. A dynamic frequency sweep test (DFST) was then made, using a constant stress of 20% of the yield stress, to determine the storage modulus (elastic modulus, $G'$) of the particle network.

Dynamic time sweep tests (DTSTs) were also performed to determine the elastic ($G'$) and loss ($G''$) moduli after different periods where the fluidized body was allowed to rest after it was vigorously stirred. The data were obtained after at fixed time intervals at a frequency of 1.0 rad/s and a stress of 20% of the initial yield stress. After one experiment was completed, the fluidized body was stirred at a high shear rate to break up any network formed after long rest periods before a second and a third DTST was performed once again.

### *2.2. Isopressing, drying and densification studies*

Only one of the slurries described above is reported here for the isopressing studies. It was formulated at pH 4 and contained 0.5 molar of ammonium chloride. After equilibration for a minimum of 24 h, the slurry was pre-consolidated by pressure filtration at 5 MPa to form a moderately high relative density compact (0.58). This was easily fluidized with vibration and had a very low shear yield stress (<45 Pa). The liquefied body was transferred to a syringe to facilitate filling the rubber mold cavity (General Electric Co., Grade RTV 644A). One mold with inner dimensions of 6.4 mm × 12.7 mm × 120 mm was used to produce rectangular bars for flexural testing. Dry alumina powder (Sumitomo, Grade AKP-15, 0.65 μm average particle diameter) was packed into one end of the mold to accommodate the liquid that was expressed during isopressing.[1] The fluidized, pre-consolidated material was extruded into the rubber mold, which was then sealed with rubber plugs and bagged to isolate the mold in the cold isostatic press (Autoclave Engineers Inc., Model IP-2-22-60). An isostatic pressure of 200 MPa was applied for 2 min to convert the fluid-like body within the mold to an elastic body.

After ejection from the rubber mold, the saturated, bar-shaped powder bodies were dried by one of three methods. (1) For the slowest drying rate, specimens were placed directly into a 70 °C oven, open to the atmosphere, for at least 24 h. (2) Rapid heating rates were applied using a thermogravimetric analyzer (TGA) (Cahn, Model TG-171) with a sufficiently large crucible and hot zone to contain a whole bar specimen. Controlled heating rates were varied from 10 °C/min to 40 °C/min, while the temperature and weight were recorded. (3) For flexure test specimens, rapid drying was performed in a medium temperature furnace (Lindberg, Blue M Laboratory Furnace, maximum temperature 1000 °C) and monitored with a thermocouple with a heating rate of 20 °C/min.

Specimen dimensions (digital calipers, Muitoyo, Model CD-6”BS) were measured at three different locations immediately after ejection from the rubber mold, and after drying at 70 °C for 24 h. Further heating to 500 °C produced a second change in weight due to the sublimation of the $NH_4Cl$ at 338 °C.[18] Specimens were observed to gain weight (≈0.25%) after cooling to ambient temperature, presumably due to the adsorption of atmospheric water. Based on continuous weight measurements, all dried flexural specimens were left in the ambient atmosphere for at least 12 h prior to testing.

Flexural testing was performed on five specimens for each condition, dried under different conditions. Two heating rates were studied: slow drying at 70 °C for 24 h, and rapid heating (20 °C/min) to 300 °C. None of these were densified at higher temperatures. The three-point flexure setup had a span of 42 mm. A mechanical testing machine (Instron Co., Model 8562) coupled with a 44.5 N (10 lb.) load cell (Eaton Corp., Model 3108-10) was used to determine the peak load at failure, and the strength was calculated by ASTM C674-88.

A specimen, dried at 70 °C, was selected to study the densification of isopressed bodies; it was cut into multiple pieces (roughly 6 mm cubes), and each was heated (Lindberg, High Temperature Furnace, maximum temperature 1700 °C) at 5 °C/min to peak temperatures of 1000 °C, 1100 °C, 1200 °C, 1250 °C, 1300 °C, 1400 °C or 1500 °C, without a dwell period. Additional specimens were heated to 1500 °C and held for 0.5 h, 1 h and 2 h. The dimensions of different specimens were measured with digital calipers before and after heating to determine their linear shrinkage. The densities of specimens after heating were also determined by the Archimedes method, in accordance with ASTM C20-92.

The sintered specimens were ground and polished to a 1 μm finish, then thermally etched at 50 °C below the densification temperature for 30 min. The grain size was determined with a field-emission scanning electron microscope (JEOL Inc., Model JSM6300F).

## 3. Results

### *3.1. Pre-consolidation and rheology studies*

Fig. 3 reports the relative density of the different pre-consolidated, saturated bodies as a function of consolidation pressure; each data point represents one experiment. As shown, the amount of salt used to formulate the slurry had an effect on the relative density. Bodies consolidated from slurries containing the lowest concentration of salt (0.1 M) were the most densely packed powder compacts (∼0.596), and were relatively independent of the consolidation pressure. Bodies consolidated from slurries containing higher salt concentrations (0.25 M, 0.5 M, and 0.75 M) had a lower relative density, but were similar (0.57–0.59) to one another, and exhibited a weak dependence on the consolidation pressure.

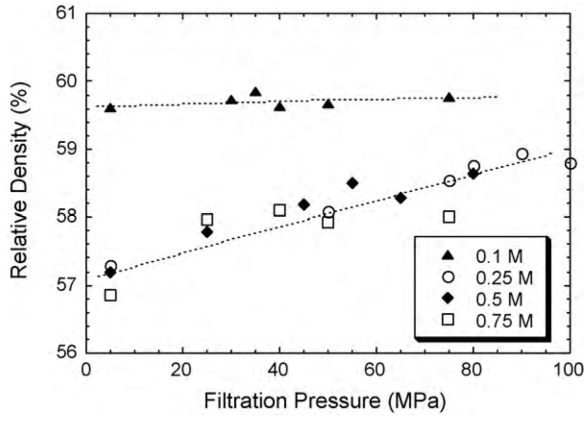

Fig. 3. The relative density of compacts formed at different filtration pressures from aqueous alumina slurries at pH 4 with 0.1–0.75 M $NH_4Cl$. Each data point represents one experiment.

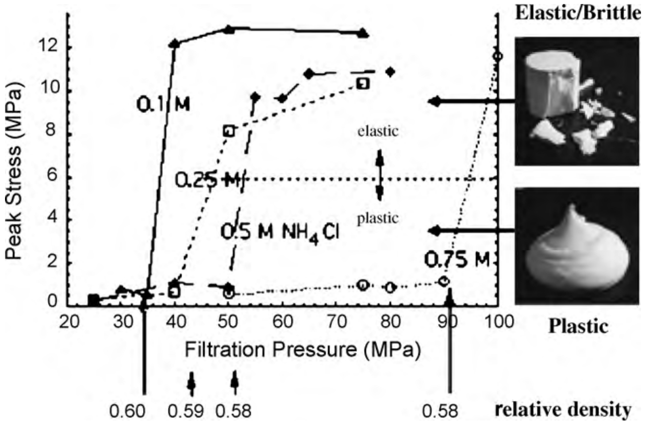

Fig. 4. The peak stresses, determined by uniaxial compression, of saturated alumina compacts with different $NH_4Cl$ concentrations, formed by pressure filtration. Specimens with peak stresses <2 MPa were plastic, whereas peak stresses >5 MPa were brittle. Each data point represents one experiment.

The peak compressive stress for all consolidated bodies is reported in Fig. 4 as a function of consolidation pressure; each data point represents one experiment. Specimens that had a relatively low peak stress (<6 MPa) exhibited plastic behavior. The inset in Fig. 4, corresponding to the plastic behavior, illustrates that these consolidated bodies could be fluidized by vibration, and then extruded. As shown with the second insert, bodies with a peak stress >6 MPa were elastic and fractured when they reached their maximum load. Every slurry with a different salt concentrations exhibited a narrow consolidation pressure range below which the compacts could be fluidized, and above which, they would fracture. Fig. 4 also shows that the relative density of the saturated bodies did not significantly change during the transition from plastic to elastic behavior.

The typical rheological behavior of a fluidized compact is shown in Fig. 5. In stress sweep experiments (Fig. 5a), the region of constant elastic modulus ($G'$) at low stresses indicates that the fluidized, consolidated body behaves much like an elastic material at low oscillatory stresses. As the stress increases, $G'$ dramatically decreased when the fluidized material began yielding. Yielding is also defined when $\tan\delta$ begins to rapidly increase ($\tan\delta = G''/G'$, where $\delta$ is the phase shift between the applied stress and the resultant strain). The frequency sweep data (Fig. 5b) shows that $G'$ is constant and much greater than $G''$ over a broad range of frequencies to confirm its elastic-like behavior; these data also produce a quantitative measure of the elastic modulus ($G'$). Table 1 reports the yield stress and elastic modulus for pre-consolidated slurries containing different amounts of salt.

Table 1
The yield stresses and storage moduli for various slurries that have been filter pressed at 5 MPa and reliquefied.

| Particle type (size, μm) | pH | $NH_4Cl$ concentration (mol/L) | Yield stress ($\tau_y$, Pa) | Elastic modulus ($G'$, kPa) |
|---|---|---|---|---|
| AKP-50 (0.25) | 4 | 0.1 | 12 | 0.9 |
| AKP-50 | 4 | 0.25 | 23 | 3.15 |
| AKP-50 | 4 | 0.5 | 42 | 7.85 |
| AKP-50 | 4 | 0.75 | 105 | 32 |

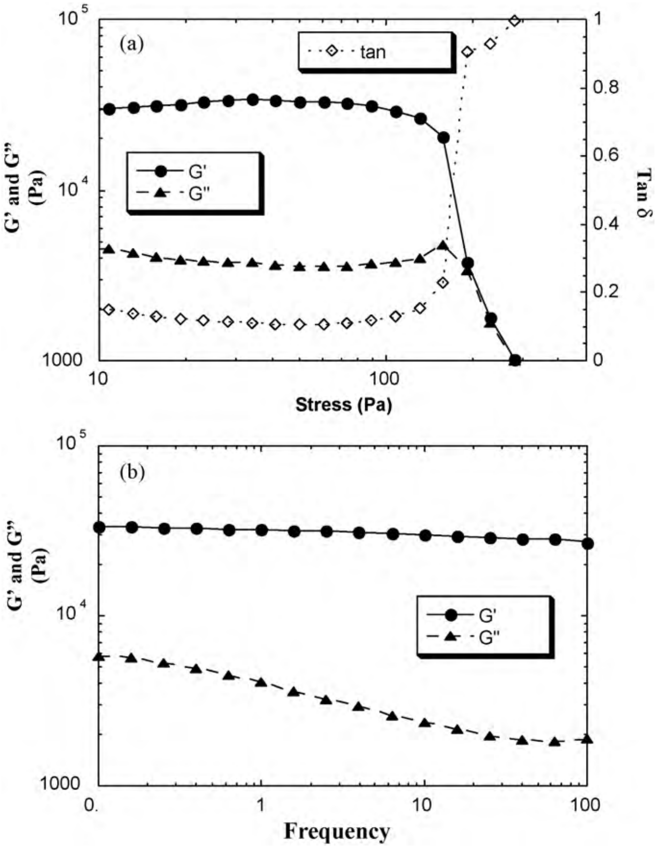

Fig. 5. Typical DSST (a) and DFST (b) data obtained for a fluidized, pre-consolidated body formulated at pH 4, 0.75 M $NH_4Cl$ and consolidated at 5 MPa. As shown in (a) the fall of $G'$ from its constant value and rise of $\tan(\delta)$ indicates that yielding has occurred at a stress of ≈105 Pa. As illustrated in (b), the much higher value of $G'$ relative to $G''$ shows that the material is elastic-like over a large range of frequency.

Fig. 6 shows the results for a pre-consolidated and fluidized slurry containing 0.5 M $NH_4Cl$ after consolidation at 5 MPa. The

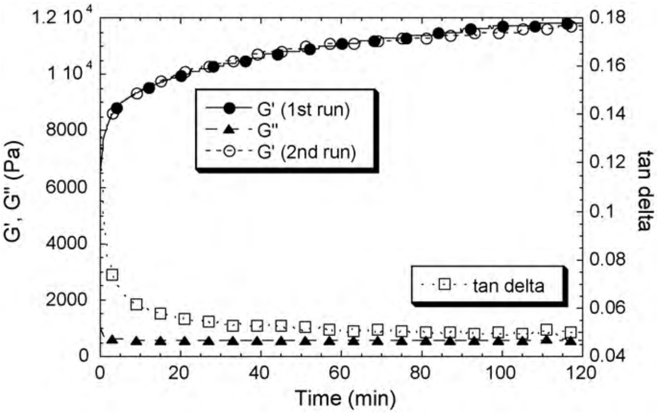

Fig. 6. Dynamic time sweep experiments repeated for an AKP-50 slurry at pH 4 and 0.5 M $NH_4Cl$ after consolidation at 5 MPa. The results from the first experiment (filled symbols and open squares for tan delta) are overlaid with the $G'$ measured for the second experiment (open circles), after the slurry had been vigorously stirred.

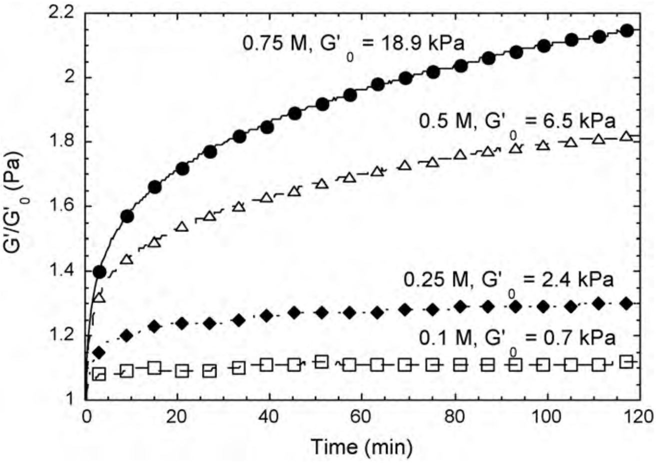

Fig. 7. Normalized DTST curves for consolidated AKP-50 slurries with varying $NH_4Cl$ concentrations: 0.1–0.75 M. The data has been normalized by $G_0'$, the initial $G'$ at the start of the experiment. The salt concentration has a strong effect on the absolute value of $G'$ as well as the time it takes to fully relax the system.

storage modulus ($G'$) and loss modulus ($G''$) were intermittently measured using DTST experiments for long periods after vigorous stirring. As shown, $G'$ initially increases rapidly with time to a relatively constant value after a long period. The increase in $G'$, and the decrease in both $G''$ and $\delta$ with time confirms that the fluid-like consolidated body becomes more elastic-like when it is allowed to relax for long periods. Fig. 6 illustrates data (open circles: 2nd run) for the same specimen after it was fully relaxed and again, vigorously stirred. The data obtained from the second experiment is nearly identical to those in the first experiment, showing that the relaxation phenomena is not an artifact (e.g., stiffening due to evaporative drying), but a real, reoccurring phenomenon. Multiple experiments produce the same conclusion.

In general, it was observed (not presented here) that the constant value of $G'$ achieved after long relaxation periods decreased with either increasing shear stress or decreasing frequency applied during the DTST experiment. The exception was when the fluidized bodies were subjected to very high frequencies (~100 rad/s for slurries with low initial storage moduli). For this case, the plateau $G'$ was significantly lower. Therefore, for consistency, all comparative data were obtained at a constant frequency (1 rad/s) and a constant relative stress (20% of the initial storage modulus).

Fig. 7 reports the relaxed elastic modulus for fluidized, pre-consolidated bodies from slurries containing different additions of $NH_4Cl$, where the elastic modulus is normalized by the initial values after vigorous stirring. These data show that the time required to recover the relaxed elastic modulus increases with added salt.

### 3.2. Isopressing, drying and densification studies

The isopressed bars were ~60 mm in length, and maintained the shape of the mold without distortion because of the very small change in volume (~8%), and thus linear dimensions (~3%), due to the small change in the relative density of the saturated bodies after pre-consolidation (0.57) versus after isopressing (0.62). Fig. 8 shows an isopressed bar and its silicon rubber mold. One end is not flat because of the powder used within the mold to absorb the expressed water during isopressing. Dimensions of the isopressed bodies were measured before and after drying. The change in length varied within ±0.05%, well within the error of the measurement; the average change in length during drying was zero.

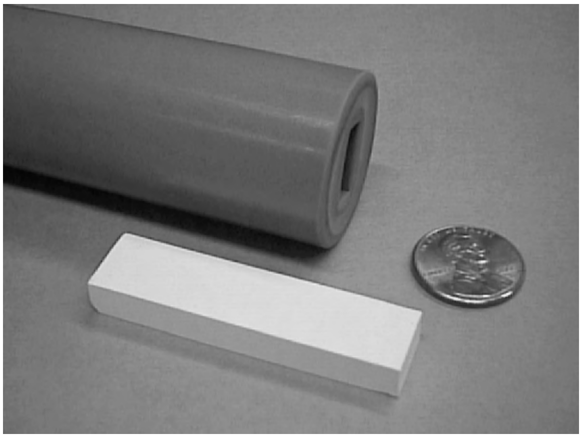

Fig. 8. Photograph of a dried, isopressed bar with the silicone rubber mold used for shaping.

Fig. 9 shows the data for the rapid, controlled rate heating was performed in the TGA at 34 °C/min. At 40 °C/min (similar, but not shown), some of the isopressed bodies fractured, presumably due to the boiling of the water within the saturated specimen. At ~34 °C/min, all specimens survived, exhibiting no cracking by visual examination. Fig. 9 shows that the specimen ceases to lose weight only after 20 min at ~34 °C/min, for a bar 6.4 mm × 12.7 mm × 60 mm. The maximum rate of weight loss was ~0.2 g/min.

The average strength for the saturated specimens and the specimens dried slowly at 70 °C and rapidly heated at 20 °C/min are listed in Table 2. The dried specimens had lower strengths relative to the saturated specimens. For the two sets of dried

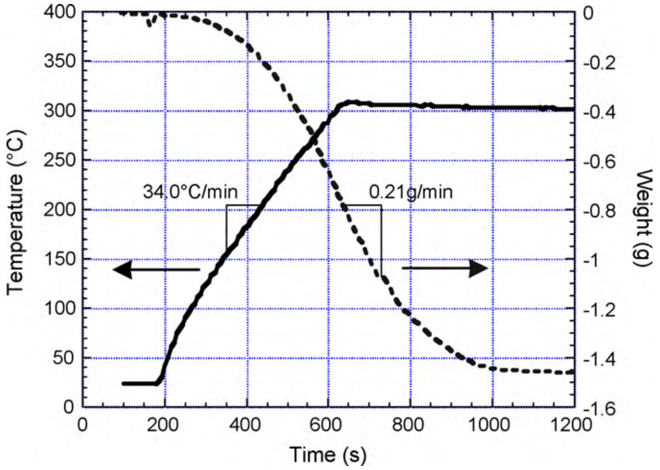

Fig. 9. Rapid drying of isopressed bars using a TGA at (a) 40 °C/min and (b) 34 °C/min. Approximately half of the specimens heated at 40 °C/min survived intact, whereas nearly all specimens dried at 34 °C/min were undamaged.

Table 2
Four point flexural strength of isopressed alumina bars, saturated, and dried either for 24 h at 70 °C or rapidly dried by heating to 300 °C at 20 °C/min.

| Tested material | Average bend strength (MPa) | Standard deviation (MPa) |
|---|---|---|
| Saturated | 3.29 | 0.33 |
| Slow drying (70 °C oven) | 1.93 | 0.27 |
| Rapid drying (20 °C/min) | 1.64 | 0.24 |

specimens, there is a slight decrease in the average strength for the bodies dried rapidly. Although the average strengths appear to depend on heating rates, yet the average values for all dried specimens were within statistical error of one another. The fracture surfaces of the dry and saturated specimens are shown in Fig. 10.

The relative density as a function of temperature for the alumina processed via Colloidal IsoPressing showed that at 1500 °C, with no hold period, the relative density was 0.985 of theoretical. The relative density increases to >0.99 when the specimens were held at 1500 °C for 0.5 h. Grain growth occurs during this period from 1.6 μm for no hold period, to 2.1 μm for a 2 h hold.

## 4. Discussion

### 4.1. Pre-consolidation and rheology studies

A major finding was that the effect of the added salt to the dispersed slurry is consistent with the interparticle pair potential shown in Fig. 1. Namely, when the concentration of salt is greater than the critical concentration (0.12 M $NH_4Cl$[15,16]) the particles form a weakly attractive particle network, and reside in the secondary minimum. As shown in Fig. 1, a potential barrier exists between the secondary and primary minimum. The slope associated with this barrier is equal to the force required to push the particles into contact. The potential well of the secondary minimum becomes deeper with increasing salt, and the resulting slope of the barrier becomes steeper. This manifests in the critical consolidation pressure required to produce an elastic body that fractures during subsequent compressive loading. Namely, as shown in Fig. 4, an increasing critical consolidation pressure is required to produce an elastic body, where the majority of particles have been pushed into contact. Below the critical consolidation pressure, a body is formed that can be fluidized. As shown in Fig. 7 and Table 1, the storage modulus (elastic modulus) and yield strength of these fluidized bodies also increases with the addition of salt, demonstrating that the weakly attractive particle network becomes more attractive.

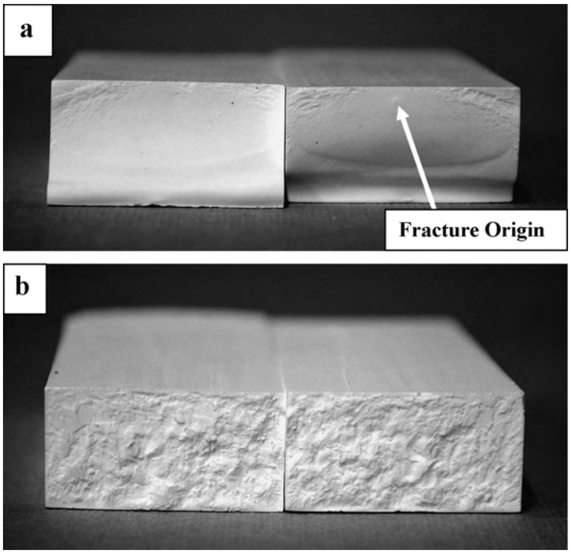

Fig. 10. Matching fracture surfaces of bars broken in bending: (a) dry and (b) saturated. Note that the fracture surface of the dry specimen reveals the fracture origin (arrow) just below the surface. It appears to be either an inclusion or an agglomerate. Such flaws could have been removed by filtering the dispersed slurry, before the addition of salt. Note that the fracture surface of the saturated body appears to have exhibited plastic deformation.

Although all of the slurries formulated for the current study are coagulated by adding salt, the one formulated at 0.1 M $NH_4Cl$ produced a high relative density that was pressure insensitive. This behavior is consistent with that reported for bodies consolidated from a dispersed slurry with the same powder used here.[13] It is interesting to note that the critical coagulation concentration, which is the lowest salt concentration that will produce an attractive particle network, has been reported to be 0.12 M $NH_4Cl$ for slurries formulated with the same powder at pH 4.[19,20] Thus, its not unexpected that the consolidation behavior of this 0.1 M slurry is similar to that of a dispersed slurry. The other slurries, formulated with larger salt contents produced nearly the same relative densities and pressure sensitivity as those reported by Franks and Lange, who formulated slurries with the same powder at pH 4 with 0.5 M and 2 M $NH_4Cl$.[12]

The change in the elastic modulus with time (Fig. 6) appears to be a new phenomenon. It is also well known that the viscosity of an attractive particle networks is time dependent, a phenomenon know as thixotropy. For thixotropic systems tested at the same final shear rate, higher viscosities are measured when the initial shear rate is at a lower value versus lower viscosities measured when the initial shear rate is higher. After the slurry is allowed to rest for some period, it recovers its higher viscosity and re-traces its shear rate thinning and hysteretic behavior. The same behavior is expected for the fluidized, weakly attractive particle networks reported here. Fig. 6 shows that the stronger of these networks, formulated with a greater salt concentration, takes a much longer period to recover its initial rheological properties, relative to the weaker networks formulated at lower concentrations of salt. Namely, it is consistent to suggest that the more strongly attractive particles will take longer to rearrange and thus produce a longer period to recover the elastic modulus of the isotropic particle network, also observed in Fig. 6.

### 4.2. Isopressing, drying and densification studies

The transformation of the fluid-like body to an elastic body, with an increased relative density from 0.57 to 0.62, obviously produces a relative density that cannot be increased further by the much smaller capillary pressures associated with drying. The 200 MPa isopressure used to achieve this high relative density is approximately 2 orders of magnitude larger than the Laplace pressure associated with capillary drying. In fact, as previously reported,[1] the relative density of bodies produced at 100–300 MPa were identical, suggesting that the relative density reported here is the maximum attainable for the powder used in these experiments.

The lack of drying shrinkage allows the saturated, consolidated body to be directly placed into the furnace used for densification without a separate drying step. The initial heating rate is only limited by the ability for water vapor to escape from the powder body without producing damage. This observation has significant consequences for the economics of colloidal powder processing.

Observations of the fracture surfaces of the saturated body strongly suggest some sort of plastic deformation occurs during crack extension. It is known that when the elastic, saturated body is subjected to large strains, the touching particle network can be pulled apart to re-establish the pair potential prior to consolidation.[4] The original short-range repulsive potential persists after consolidation, thus allowing the body to be liquefied.[12] For example, although unreported, this can be done by repeatedly hammering the pieces of the elastic body contained within a plastic bad to prevent drying, i.e., high stresses can convert the elastic body into a fluid-like body. This observation, although implemented with crude experimental tools, strongly suggests that particles within a small zone surrounding the tip of an extending crack can be fluidized. The fluidized material around the crack will absorb energy during fracture. This argument suggests that the higher strength of the saturated body, relative to the dry body, is caused by the larger crack growth resistance of the saturated body. Further experiments are needed to examine this hypothesis.

The densification of isopressed bodies is improved due to their high relative density. This allows the isopressed compacts to achieve near theoretical density a lower temperatures and for shorter heat treatment periods. Therefore, the grain growth expected at higher temperature and for long dwell periods will be minimized, resulting in a finer microstructure.

## 5. Conclusions

The consolidation of a dilute slurry to form a highly concentrated slurry is an important step in the Colloidal IsoPressing forming method. In the aqueous alumina system reported here, we control the interparticle interaction with the addition of acid (pH 4) to first form a dispersed slurry, then the addition of excess electrolyte (salt) to form a short-range interparticle repulsive potential. The short-range repulsion prevents a majority of particles from being pushed into contact at low consolidation pressures, enabling the consolidated body to be fluidized. The concentration of salt, in the range studied, has been shown to weakly affect the relative density of the compacts formed during pressure filtration. The plastic to elastic transition was dependent on the relative density achieved during consolidation and the strength of the attractive particle network. The rheological behavior of fluidized consolidated bodies can be characterized with dynamic techniques. We report that the storage modulus and yield stress, both of which are related to the strength and density of the particle network, are affected by the salt concentration. The time dependent behavior of the fluidized, consolidated bodies can be explained by the relaxation of the anisotropic particle network that develops during flow at high shear rates into an isotropic structure that is recovered after long periods of rest. Isopressing rapidly converts the fluid-like body into an elastic body and also increases the relative density. We demonstrate that the saturated, isopressed body does not shrink during drying, enabling rapid drying during heating to the densification temperature.

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