

The effect of soluble sulfate concentration on the rheological behavior of nanoparticulate titania suspensions

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Two variants of a nanoparticulate titania were investigated for their rheological behavior. These powders were synthesized via a sulfuric acid process, where modification of particular parameters resulted in powders varying in residual sulfate level. It was assumed that residual sulfate would affect the agglomerate structure of suspensions of these powders. These powders were washed with distilled deionized water to remove as much residual soluble sulfate as possible and the supernatant tested for sulfate level and pH. Microstructural and rheological behavior of the powders were examined as a function of number of washes. The rheological yield point was determined to increase with number of washes and in turn increase with decreased residual sulfate level.

Key words: Agglomeration/Agglomerates, Rheology/Rheometry, Titanium Dioxide.

Introduction

Nanoscale titania powders are gaining attention in many applications, particularly as extruded catalyst monolith honeycomb substrates. As the demands for finer geometry for optimal use grows, flow behavior and shape retention become concerns. Extrudability is assessable via rheological behavior, which can be shown to be controlled by agglomerate structure, a parameter which is controlled by the nature of the base powder itself. In this exploration, the effect of residual sulfate ions upon agglomerate structure and in turn rheological behavior were examined.

The powder investigated here was a titania manufactured by a sulfuric acid process. This process involves taking ilmenite (or a suitably titanium-rich ore) and agitating it in a sulfuric acid bath. The resultant cake is dissolved and treated to remove any impurities before crystallization of titania crystals, which are then washed to remove any residual impurities [1]. This process involves multiple parameters, such as crystallite seeding, pH, washing volume and calcination temperature. The modification of these parameters creates variants in powder properties, one of which being a varying amount of residual sulfate remaining in the powder.

The residual sulfate in the powders contributes to agglomeration according to the DLVO Theory. Van der Waals forces will attract primary crystallites when they are close to one another. Counteracting the van der Waals forces will be Coulombic forces, created by the

interaction of sulfate ions. The soluble sulfate ions will be attracted to primary crystallites of titania, forming a counterion cloud around the crystallite. The radius from the surface of the crystallite to the edge of the counterion cloud, known as the double layer thickness, is critical in the formation of agglomerates. When the double layer is thick enough, the van der Waals forces will be too weak to attract the crystallites together, and the Coulombic forces experienced by the similarly-charged counterion clouds will repel crystallites from one another [2, 3]. As a relatively large ion and as a strong potential-determining ion, sulfate will greatly affect the double layer thickness of the crystallites and in turn the Coulombic forces experienced [4]. From this it is inferred that increasing levels of soluble sulfate can be predicted to reduce agglomeration in a suspension.

It has been shown that agglomeration in suspensions of ceramic powder will have a marked effect upon both the yield pressure of the suspension and the density of a resulting cast. Suspensions with large agglomerates will experience relatively high yield pressures, which in turn will force the rheological behavior of the suspension at slow flow rates to be extremely dependent upon agglomeration. At the same time, suspensions with agglomerates that are too large have been shown to produce casts with low density [5]. Niesz and Bennett have reported that agglomeration also greatly affects microstructure developed during processing, with large agglomerates resulting in non-uniform microstructures consisting of both coarse and fine particles [6].

In suspensions of sufficiently high concentration the agglomerates will connect to form a gel-like structure. The bonding within this structure can be assessed by dynamic stress rheometry (DSR). DSR can be used to

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simulate shear conditions that a suspension will experience during processing or in undergoing a forming technique such as extrusion. A suspension will yield when the stress overcomes the bonding forces and breaks down agglomerates, letting the crystallites begin to flow separately from one another, in turn breaking the gel-like structure. Rheological profiles obtained from dynamic stress rheometry can be used to compare the strength of bonding between agglomerates for different powders with different levels of residual sulfate [7]. It is the purpose of this investigation to examine high and low sulfate titanias and the effect of washing and sulfate removal on their agglomerate characteristics.

Experimental

Titania was obtained at high and low levels of residual sulfate. The powders were made to a 22.5 weight percent solids loading suspension in distilled deionized water and ultrasonically mixed for two minutes. After ultrasonication, the suspensions were centrifuged for 10 minutes at 5000 RPM and 10°C in a Beckman J2-21M Centrifuge. A 50 ml sample of supernatant was decanted from the centrifuged samples and saved for further experimentation, with samples of the centrifuged powder cakes saved after 1, 3, and 5 washes for rheological studies and imaging via scanning electron microscopy (SEM). Those cakes not saved for rheological studies were remade to 22.5 weight percent solids loading, ultrasonicated for two minutes, and centrifuged again, up to a total of 5 wash cycle iterations.

The decanted supernatants were tested for sulfate level on a Betz DR/2000 Spectrophotometer and pH on a Fisher Scientific Accumet Model 25 pH/Ion Meter. A spectrophotometer will record the intensity of light transmitted by a supernatant and compare that value to the intensity of light transmitted when that supernatant has been reacted with a precipitant. These intensities, when compared with standard solutions of known ion level, can be used to find the amount of that ion present in a liquid in mg/l. The spectrophotometer was calibrated using Hach Sulfate Standard Solutions according to the Betz DR/2000 calibration instructions supplied by the Hach Company. Two samples were made of 1 ml of supernatant diluted to a 25 ml sample with distilled deionized water. One sample was used as a zero for the spectrophotometer while the other was reacted with a Hach Barium Chloride Powder Pillow to precipitate sulfate out of the sample. The test sample was then placed in the spectrophotometer to take sulfate readings, and these values were used to back calculate total sulfate levels after washing in parts per million (ppm). The remaining supernatant was then used for pH measurements with the Accumet Model 25 pH/Ion Meter.

The rheological behavior of the centrifuged powder cakes was determined using dynamic stress experiments

on a TA Instruments AR-1000N Rheometer. The cakes were made to 22.5 weight percent solids loading in distilled deionized water and subjected to an oscillatory stress sweep test. This test then provided Elastic Modulus (G') and Viscous Modulus (G'') data, which have been shown to be measures of the proportionality between the stress applied to a body and the strain it experiences (G') and energy lost per unit volume with consecutive stress cycles (G'') [8]. The yield point of these suspensions is assumed to be the intersection between the two moduli curves. Samples were also taken from the cakes and dried for 24 hours on SEM studs to minimize drying effects for microscopy studies on a Leo-Zeiss Gemini 982 Field Emission Scanning Electron Microscope. The in-lens detector was used to obtain greater resolution, with a working distance of 5 mm and an accelerating voltage of 10 kV.

Results & Discussion

Residual sulfate levels after washing of the powders can be seen in Table 1. As the low sulfate had a manufactured residual sulfate level of approximately 8,000 ppm and the high sulfate approximately 30,000 ppm, it was possible to determine a percentage decrease in sulfate for each wash. After one wash, about 55% of the residual sulfate could be removed; after two washes, 83% of the residual sulfate could be removed; and after three washes, 93% of the residual sulfate could be removed. After three washes, the sulfate level of the low sulfate powder became very low and indeterminable by the methods used in this experiment. However, the high sulfate powder experienced a decrease in residual sulfate of 96% after four washes, and 97% after five washes. It was observed that after the high sulfate powder was washed three times, its residual sulfate levels began to resemble that of the low sulfate powder after one wash, and similarly for the four and five wash readings in high sulfate powder compared to the two and three wash readings in the low sulfate powder.

The pH levels of the powders can also be seen in Table 1 as a function of washing cycles. Notable is how the high sulfate powder after three washes resembles the low sulfate powder after one wash, and how both powders tend towards a pH of 4, the isoelectric point of rutile, with increasing number of washes. Due to sulfate

Table 1. Soluble Sulfate Content and pH as a function of washing

Number of Washes	Soluble Sulfate (ppm)		pH	
	Low	High	Low	High
1	3777	12777	1.89	1.50
2	1444	4888	2.18	1.80
3	611	2111	2.46	2.04
4		1166	2.87	2.25
5		722	3.22	2.42

being a strong potential-determining ion, it is no surprise that the pH increases as sulfate is removed through the washing of the powders.

Figures 1, 2, and 3 depict the microstructures of the low sulfate powder after one, three, and five washes, respectively. Figures 4, 5, and 6 similarly depict the

microstructures of the high sulfate powder after one, three, and five washes, respectively. In the low sulfate powder, there was observed a slight increase in agglomerate size from 1 to 3 washes, increasing from approximately $1\ \mu\text{m}$ to $1.2\ \mu\text{m}$, with finer agglomerates present as well. After the low sulfate powder was

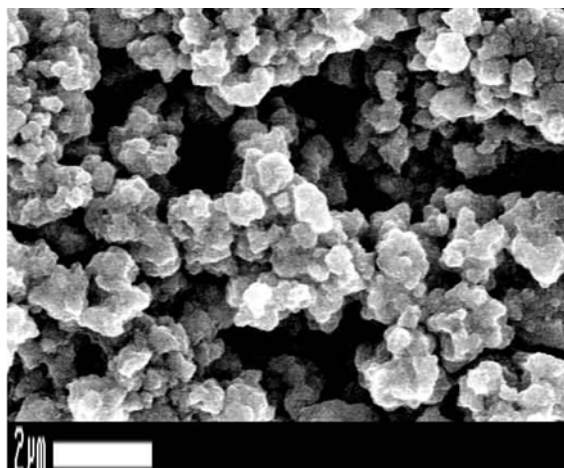


Fig. 1. Microstructure of low sulfate powder after one wash.

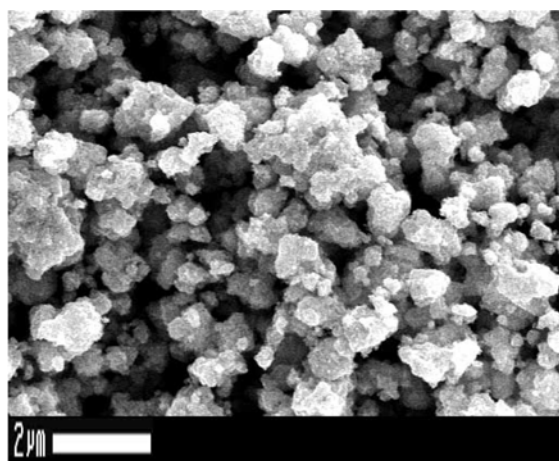


Fig. 4. Microstructure of high sulfate powder after one wash.

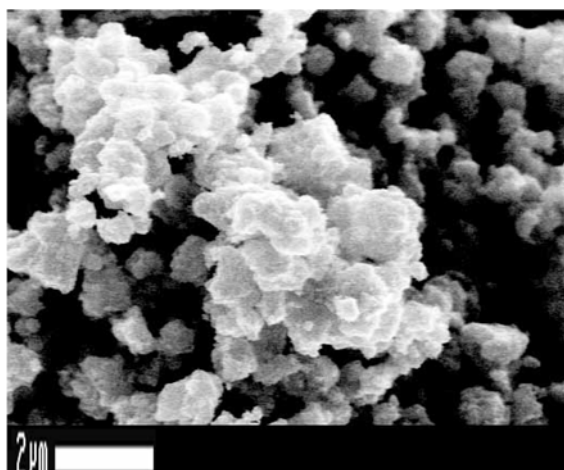


Fig. 2. Microstructure of low sulfate powder after three washes.

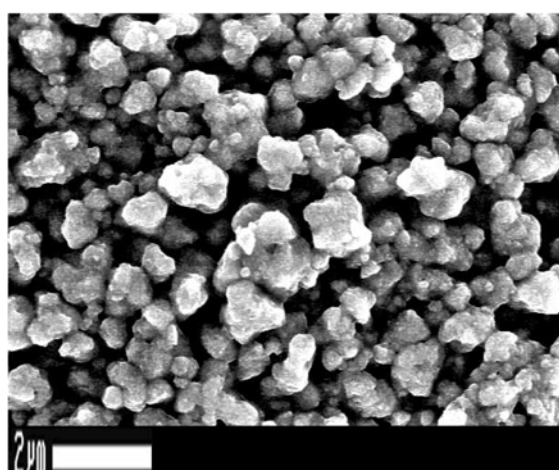


Fig. 5. Microstructure of high sulfate powder after three washes.

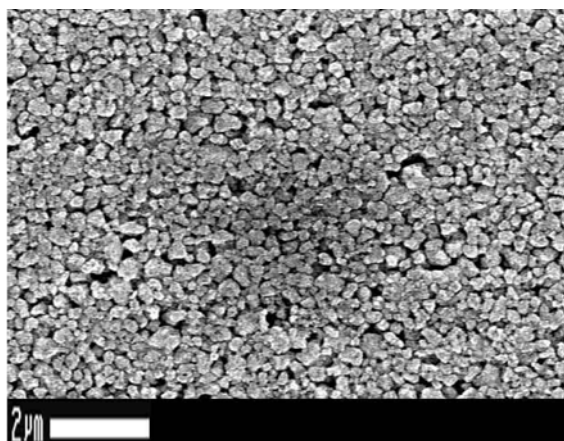


Fig. 3. Microstructure of low sulfate powder after five washes.

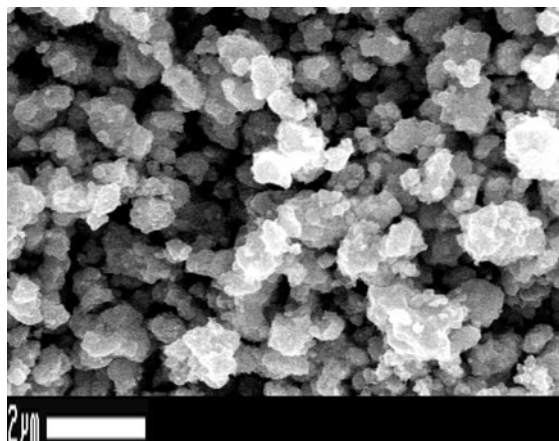


Fig. 6. Microstructure of high sulfate powder after five washes.

washed five times, at which point the sulfate level became indeterminable, the agglomeration of the powder drastically decreases as the agglomerates become much more dispersed and reduce to a size of approximately 300 nm with little sign of nonuniformity in agglomerate size. The high sulfate powder experienced only an increase in agglomerate size as a function of the washing of the powders, with coarse agglomerates increasing from approximately 750 nm after one wash, 1 μm after three washes, and 1.1 μm after five washes. As residual sulfate was removed from the powders, the counter-ion clouds surrounding each primary crystallite became smaller and smaller, allowing them to come much closer together and larger agglomerates to form due to reduced electrostatic repulsion. The change in agglomerate size appeared to depend on how much residual sulfate was present before washing, as after washing a powder with less than 4000 ppm of residual sulfate, the change in agglomerate size reduced. Once again, it was notable how after three washes the microstructure of the high sulfate powder began to resemble the microstructure of the low sulfate powder after one wash.

The powders were subjected to dynamic stress rheometry to determine the rheological behavior and yield point of each, with the yield point taken to be the intersection of the Elastic Modulus and Viscous Modulus curves, and the yield regime the area over which a drop in moduli of three orders of magnitude was experienced. Figure 7 shows the initial rheological behavior of the low sulfate powder, with a yield point of approximately 0.7 Pa. In Figure 8, it can be seen that after one wash the low sulfate powder experienced a slight increase in

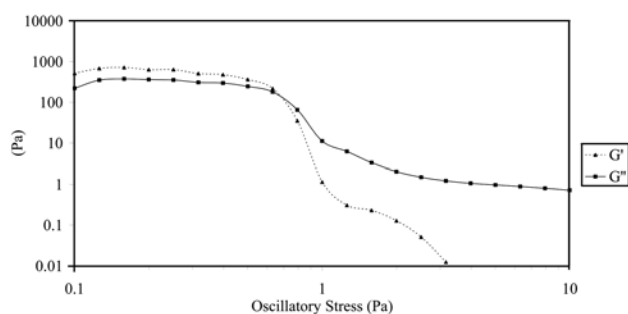


Fig. 7. Initial rheological behavior of low sulfate powder.

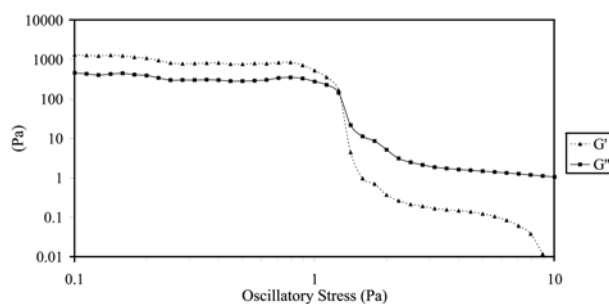


Fig. 8. Rheological behavior of low sulfate powder after one wash.

yield point, to 1.0 Pa. Similarly, the high sulfate powder experiences an increase in yield point with washing.

Figures 9-12 show the rheological behavior of the high sulfate powder after no washes, one, three, and five washes, respectively. Initially, the high sulfate powder had a very low yield point, less than 0.1 Pa,

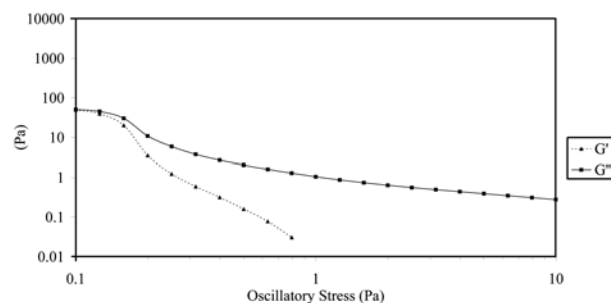


Fig. 9. Initial rheological behavior of high sulfate powder.

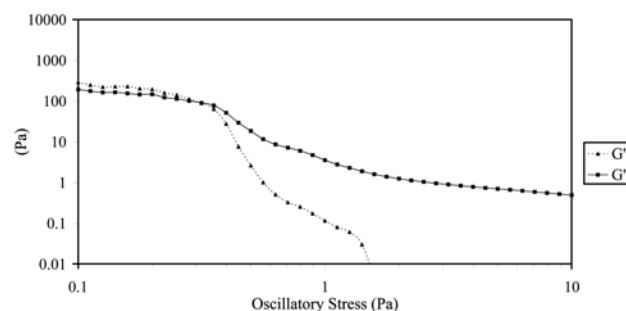


Fig. 10. Rheological behavior of high sulfate powder after one wash.

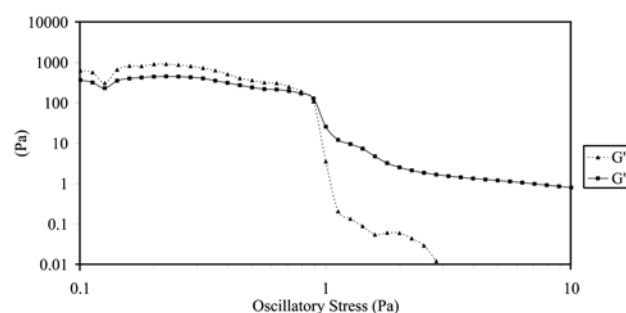


Fig. 11. Rheological behavior of high sulfate powder after three washes.

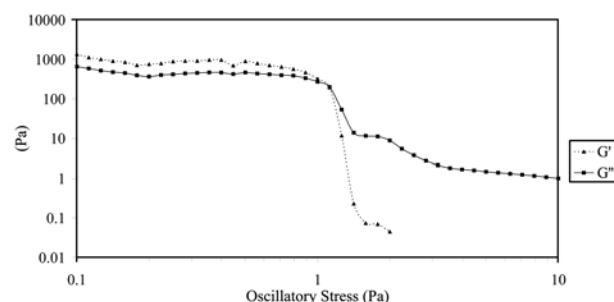


Fig. 12. Rheological behavior of high sulfate powder after five washes.

with a very broad and vague yield regime. However, after one wash, the yield point increased to 0.3 Pa and the yield regime became tighter. This trend increased with washing, with yield points of 0.9 Pa and 1.0 Pa experienced after three and five washes, respectively, with the yield regime narrowing and becoming much more defined with increasing washing. As residual sulfate was removed from the powders, larger agglomerates were formed in suspension, which then resulted in a non-uniform microstructure that contained more large particles. These particles controlled the yield regime rather than the fine particles, and resulted in the yield regime becoming more defined with larger agglomerates. The increase in yield point corresponds to the increase in agglomerate size of the powders, as a larger agglomerate will require more force to break apart. Again, after washing the high sulfate powder three times, a rheological behavior was observed that was similar to that of the low sulfate powder after one wash.

Conclusion

Nanoparticulate titania powders with high and low levels of residual sulfate were examined. The powders were subjected to a series of washing cycles at 22.5 weight percent solids loading in an attempt to remove soluble sulfate. It was observed that after three washes, approximately 93% of residual sulfate could be removed from the powder. The reduction in sulfate in the powders affected the agglomeration characteristics of

the powders, in turn affecting the yield behavior of the powders. It was then determined that washing the powders can be used to control the yield behavior of the powders, resulting in a more well-defined yield regime with increasing washes and decreasing residual sulfate. In effect, the variable process history of the powders was circumvented by washing the powders to a similar level of residual sulfate.

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