Rheological Characterization and Extrusion of Suspensions of Natural Zeolites

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Abstract:
A rheological characterization and extrusion of aqueous suspensions of natural zeolites were carried out in this work. Preparation of suspensions followed similar routes to those used for the colloidal processing of ceramic powders. The suspensions were prepared at different volume fractions (v/v%) ranging from 5 to 61 v/v% for a pH value of 7. The suspensions showed a Newtonian behavior for solid contents up to 20 v/v% and shear thinning at higher solid loads. For solid contents above 35 v/v%, the suspensions exhibited hysteresis and a yield stress that growth exponentially with the solid load. The appearance of a yield stress and its fast growing at relatively low solid concentration, as compared to other type of ceramic suspensions, is attributed to several factors as inter-particle interactions, the presence of relatively large particles and to the influence of their irregular morphology. Also, a breaking stress was measured for solid contents above 35 v/v%, which characterizes a failure of the structure of the suspensions after yielding. This breaking stress determines the onset of slip flow of the suspensions, which is interpreted in this work as a signal of good extrusion characteristics. Finally, inexpensive and free of surface defects tubes were obtained from natural zeolites.

Zusammenfassung:
Eine rheologische Charakterisierung und Extrusion wässriger Suspensionen natürlicher Zeolithe wurden in dieser Arbeit durchgeführt. Bei der Herstellung der Suspensionen wurden ähnliche Methoden angewandt wie bei der kolloidalen Verarbeitung von keramischen Pulvern. Die Suspensionen wurden bei unterschiedlichen Volumenanteilen (v/v%) hergestellt, die von 5 bis 61 v/v% bei einem pH-Wert von 7 reichten. Die Suspensionen wiesen ein Newtonsches Verhalten bei einem Füllstoffgehalt bis 20 v/v% und strukturviskoses Verhalten bei höheren Füllstoffgehalten auf. Für Füllstoffgehalte oberhalb von 35 v/v% wiesen die Suspensionen Hysteresis und eine Fließgrenze auf, die exponentiell mit dem Füllstoffgehalt wuchs. Das Auftreten einer Fließspannung und ihr ausgeprägtes Wachstum bei relativ niedrigen Füllstoffkonzentrationen, verglichen zu anderen keramischen Suspensionen, wird verschiedenen Faktoren zugeschrieben wie den Partikel-Partikel-Wechselwirkungen, der Gegenwart von relativ großen Partikel und des Einflusses ihrer heterogenen Morphologie. Darüber hinaus wurde eine Bruchspannung für Füllstoffgehalte oberhalb von 35 v/v% gemessen, die ein Versagen der Struktur der Suspension oberhalb der Fließgrenze andeutet. Die Bruchspannung bestimmt den Beginn des Gleitfließens der Suspensionen, was in dieser Arbeit als ein Kennzeichen für gute Extrusionseigenschaften gedeutet wird. Kostengünstige und von Oberflächendefekten freie Röhren wurden mit natürlichem Zeolith erhalten.

Résumé:
Une caractérisation rhéologique et l'extrusion de suspensions aqueuses de zéolites naturelles ont été entreprises dans ce travail. La préparation des suspensions est semblable à celles utilisées pour le traitement colloïdal des poudres de céramique. Les suspensions ont été préparées à des fractions volumiques différentes allant de 5 à 61 %v/v et à un pH 7. Les suspensions présentent un comportement Newtonien pour des fractions solides allant jusqu'à 20 %v/v, et rhéo-amincissant pour des fractions supérieures. Au-dessus de 35 %v/v, les suspensions montrent une hystérésis et une contrainte seuil qui croît exponentiellement avec la charge solide. L'apparition d'une contrainte seuil et sa croissance rapide pour des concentrations relativement faibles en solide par rapport à d'autres types de suspensions céramiques, sont attribuées à différents facteurs tels que les interactions inter-particules, la présence de particules relativement grandes, et à l'influence de leur morphologie irrégulière. De plus, une contrainte de fracture a été mesurée pour des fractions en solide supérieures à 35 %v/v, qui caractérise la rupture de la structure des suspensions au-dessus du seuil. Cette contrainte de fracture détermine le début de l'écoulement de glissement des suspensions, qui est ici interprété comme un signe de bonnes caractéristiques d'extrusion. Enfin, des tubes peu coûteux et sans défauts de surface ont été obtenus à partir de zéolites naturelles.

Key words: powder suspensions, natural zeolites, extrusion, yield stress

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The extrudates obtained by using the binder also appeared free of surface defects, but in contrast to the observed for the suspension without binder, these retained their shape after extrusion, in agreement with a higher yield stress value (see Figure 10b). The three different extrusion speeds used resulted in tubes of similar quality. Still, further work is necessary to establish the minimum binder concentration required to reach a critical yield stress that maintains the extrudate shape with the minimum extrusion pressure. At this point, however, the present study shows that the procedure followed in this work to prepare suspensions and pastes of natural zeolites allows for the production of inexpensive and free of surface defects extrudates. Further work is being carried out to evaluate the physical-chemical properties of the tubes.

4 CONCLUSIONS

The results in this work show several aspects of the rheological behavior of suspensions of natural zeolites, which are explained on the basis of their particle size distribution and morphology. The main conclusions are listed below:

- The suspensions showed Newtonian behavior for solid content up to 20 v/v% and shear thinning at higher solid loads. For solid contents above 40 v/v%, the suspensions exhibited viscoplastic behavior, hysteresis and yield stress. The appearance of a yield stress limits the slip casting processing of this sort of suspensions.
- The concept of a "breaking stress" was introduced for solid contents above 40 v/v%, which characterizes a sudden failure of the structure of the suspensions after yielding. The "breaking stress" determines the onset of slip and plug flow, which are interpreted as signals of good extrusion characteristics of the suspensions.
- Both, the yield and breaking stresses grow exponentially with the solids loading.
- Finally, the results from this work may be useful for understanding the rheological behavior of suspensions of natural zeolites and its influence during processing. A successful application of the results has been made to the extrusion of tubes made up of MNZ.

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REFERENCES

[1] Breck DW: Zeolite molecular sieves. Structure, chemistry and use, John and Wiley and Sons, New York (1974).

[2] Roskill Information Services Ltd: The economics of zeolites, First Edition, London (1988).

[3] Rakovan J: Zeolite, Rocks and Minerals. 79 (2004) 271–743.

[4] Watanabe Y, Yamada H, Kokusen H, Tanaka J, Moriyoshi Y, Komatsu Y: Ion exchange behavior of natural zeolite in distilled water, hydrochloric acid, and ammonium chloride solution, Sep. Sci. Technol. 38 (2003) 1519–1532.

[5] Corma A: Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions, Chem. Rev. 95 (1995) 559–414.

[6] Thomas FD Jr: Applications of zeolites in petroleum refining, Topics Catalysis. 13 (2000) 349–356.

[7] Mumpton FA: La roca magica: Uses of natural zeolites in agriculture and industry, Proc. Natl. Acad. Sci. USA. 96 (1999) 3463–3470.

[8] Englert AH, Rubio J: Characterization and environmental application of a Chilean natural zeolite, Int. J. Miner. Process. 75 (2005) 21–29.

[9] Katsoulos PD, Panousis N, Roubies N, Christaki E, Karatzias H: Effects on blood concentrations of certain serum fat-soluble vitamins of long-term feeding of dairy cows on a diet supplemented with clinoptilolite, J. Vet. Med. A. 52 (2005) 157–161.

[10] Mumpton FA, Fishman PH: The application of natural zeolites in animal science and aquaculture, J. Anim. Sci. 45 (1977) 1188–1203.

[11] Ostrooumov M, Ostrooumova I: First reported occurrence of clinoptilolite-rich tuff deposits in the Mexican Volcanic Belt (state of Michoacan, Southwestern Mexico), Zeolite '06–7th International Conference on the Occurrence, Properties, and Utilization of Natural Zeolites, Socorro, New Mexico, USA (2006).

[12] Large FF: Powder processing science and technology increased reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.

[13] Hernández N, Sánchez-Herencia AJ, Moreno R: Forming of nickel compacts by a colloidal filtration route, Acta Mater. 53 (2005) 919–925.

[14] Sing BP, Menchavez R, Takai C, Fuji M, Takahashi M: Stability of dispersions of colloidal alumina

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http://www.appliedrheology.org

particles in aqueous suspensions, J. Colloid Interface Sci. 29 (2005) 1181–186.
[15] Lewis JA: Colloidal Processing of Ceramics, J. Am. Ceram. Soc. 83 (2000) 2341–2359.
[16] Davis J, Binner JGP: The role of ammonium polyacrylate in dispersing concentrated alumina suspensions, J. Eur. Ceram. Soc. 20 (2000) 1539–1553.
[17] Luckman P, Ukeje M: Effect of particle size distribution on the rheology of dispersed systems, J. Colloid. Interface Sci. 220 (1999) 347–356.
[18] Lam YC, Wang ZY, Chen X, Joshi SC: Wall slip of concentrated suspension melts in capillary flows, Powder Technol. 177 (2007) 162–169.
[19] Graczyk J, Gleissle W: Rheology and extrudability of ceramics compounds, Appl. Rheol. 3 (1993) 28–38.
[20] Li YY, Perera SP, Crittenden BD, Bridgwater J: The effect of the binder on the manufacture of a 5A zeolite monolith, Powder Technol. 116 (2001) 85–96.
[21] Madhusoodana CD, Das RN, Kameshima Y, Okada K: Preparation of ZSM-5 zeolite honeycomb monoliths using microporous silica obtained from metakaolinite, J. Porous Mater. 12 (2005) 273–280.
[22] Zhang X, Meng G, Liu X: Preparation and characterization of tubular porous ceramics from natural zeolita, J. Porous Mater. 15 (2008) 101–106.
[23] McIntyre EC, Filisko FE: Squeeze flow rheology of zeolite suspensions, Appl. Rheol. 19 (2009) 44322.
[24] Van Hooff JHC, Roolefson JW in: Introduction to Zeolite Science and Practice: Studies in Surface Science and Catalysis, 58, Elsevier, Amsterdam (1991) 241.
[25] Ersoy B, Çelik MS:Electrokinetic properties of clinoptilolite with mono-and multivalent electrolytes, Microporous Mesoporous Mater. 55 (2002) 305.
[26] Pavlínek V, Sáha P, Pérez-González J, de Vargas L, Stejskal J, Quadrat O: Analysis of the yielding behavior of electrorheological suspensions by controlled shear stress experiments, Appl. Rheol. 16 (2006) 14–18.
[27] Paumier S, Pantet A, Monnet P, Touze-Folts N: Evaluation of the viscoelastic properties of a clay material using a flow curve, App. Rheol. 19 (2009) 23824.
[28] Ancey C, Jorrot H: Yield stress for particle suspensions within a clay dispersion, J. Rheol. 45 (2001) 297–319.
[29] Tong J, Chen D: Preparation of alumina by aqueous gelcasting, Ceramics Inter. 30 (2004) 2061–2066.
[30] Benbow J, Bridgwater J: Paste flow and extrusion, Clarendon Press, Oxford (1993).

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