Study of different deflocculation mechanisms on a porcelain ceramic paste

E. Barrachina, J. Llop, M. Notari, D. Fraga, R. Martí, I. Calvet, A. Rey,
T. Stoyanova Lyubenova, S. Kozhukharov, V. Kozhukharov, J. Carda

Abstract:*The need of optimizing the spray-drying process in the traditional ceramic industry has caused the development of a huge number of commercial deflocculants, able to improve the rheology of concentrated suspensions. This work is focused on the study of 4 commercial liquid deflocculants for stabilizing suspensions using different mechanisms to avoid flocculation. A 70%-solid content suspension of a porcelain composition has been deflocculated with each deflocculant (“A”, “B”, “C” and “D”) and values of pH, conductivity, particle size distribution and viscosity and thixotropy at a specific shear rate, have been measured for each sample.*

Key words: *Spray-drying process, rheological properties, deflocculant, viscosity, thixotropy, flocculation, suspensions.*

INTRODUCTION

In the ceramic sector, the spray-drying factories tend to use high solid content suspensions to increase the production efficiency and reducing energy consumption [1], [2]. The dispersion of ceramic particles is a fundamental step in the industrial ceramic processes in order to obtain a homogeneous and stable system of elementary particles [3]. Currently, inorganic substances (as silicates, phosphates and carbonates sodium salts) or organic additives, generally polyacrylate salts with different molecular structures, are commonly used in liquid state. They are added in a percentage between 0.1 wt% and 0.6 wt%, to lower the viscosity typically around 200-400 mPa.s [4].

There are basically three mechanisms which act individually or in combination depending on the deflocculant used [5, 6]:

- Electrostatic Action: cation exchange and, thus, an effect on the thickness of the electrical double layer of the raw materials particles.
- Steric Hindrance: steric repulsion by the introduction of functional groups which act as spacers between the raw material particles.
- Cation capture: binding of interfering cations by complexing.

The aim of the present research is to compare the rheological effect of different mechanisms of deflocculation on a porcelain ceramic standard composition, using four commercial liquid deflocculants, which exhibit preferential action mechanisms [7, 8].

EXPERIMENTAL

Commercial Tested Deflocculants

Four commercial deflocculants with different mechanisms of particle dispersion have been selected and they are specified in Table 1. “A”, “B” and “C” contain silicate (sodium silicate), whereas “D” contains only phosphonates. On the other hand, “A” and “B” act according to the mechanism of charges and steric effect, while “C” uses charges and complexant effect and “D” stabilizes suspensions by means of the complexant effect. These deflocculants have been supplied by the international company Zschimmer&Schwarz. The analysis of the deflocculants consists of measuring their pH and the electrical conductivity.

Table 1. Types of the used Deflocculants.

Deflocculant	Composition	Mechanism
A	Silicate with polymer	Charges and steric effect
B	Silicate with polymer	Charges and steric effect
C	Silicate with phosphonates	Charges and complexant effect
D	Phosphonates	Charges and complexant effect

Suspensions preparation

The suspensions prepared have consisted of a standard porcelain spray-dried powder mixed with water (70%-solid content) and different type and amount of deflocculant. They have been milled during 7 minutes in a planetary alumina ball mill to achieve 100% particles under 63 micrometers such as the industrial milling process for porcelain pastes.

Suspensions Characterisation Techniques

In each case, the solid content, measured from the difference between wet and dried weight of a sample of slip, and the size particle distribution, by means of a LS 13 320 Laser Diffraction Particle size analyser of Beckman Coulter, have been measured in this study, in order to control the modification of size distribution with the variation of rheological properties.

The electrolytical parameters have been tested by a Eutech pH6+ and a Eutech Cond7. The rheological variables of each suspension have been obtained from a traditional control rate mode, which performs seven subsequent stages, shown in Table 2, measured by a Haake Viscotester 550.

Table 2. Control rate mode programme

Rotation speed (s^{-1})	Duration (s)
0-1000	120
0-0	1
1000-0	120
0-0	1
0-1000	120
0-0	1
1000 – 0	120

The first rheometrical cycle has been used to homogenize the testing time of all the suspensions and, hence, the viscosity and thixotropy have been extracted from the second cycle. The viscosity has been studied at two different shear rate (low shear rate, 100 s^{-1} and high shear rate, 1000 s^{-1}). The lowest shear rate simulates the emptying of the industrial ball mills, while the highest one is similar to the rate used during the spray-drying operation. The magnitude of thixotropy has been determined making use of a CR-rheometer and evaluating the hysteresis area contained in between the flowability curves (shear stress or shear rate) of the second cycle [9].

RESULTS AND DISCUSSION

Commercial Tested Deflocculants

The conductivity of the investigated deflocculants belongs to 35 - 50 mS/cm range. All silicate containing deflocculants (“A”, “B” and “C”) reveals strong alkalinity, possessing pH values about around 12, while the purely phosphonate one (“D”) shows slightly lower pH values, around 10.5 (Fig.1).

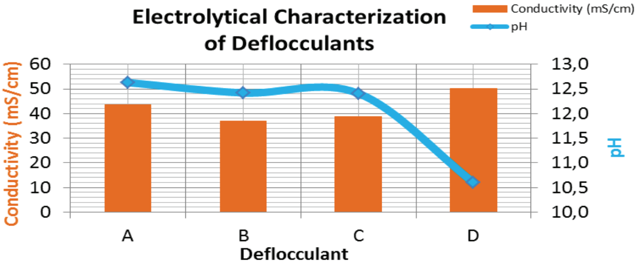

Fig.1. Electrical characteristics of the investigated deflocculants.

Measurements

The average of the solid content obtained is 70.08 ± 0.15 wt% inside the available range of high industrial values and the standard deviation is enough narrow to compare the different prepared suspensions. The particle size distribution did not varied with the deflocculant content of the corresponding suspensions. The mean value was about 15 μm.

About the electrolytical parameters, the electrical conductivity is directly proportional to the percentage of deflocculant content and the total values range is 5,0-6,1 mS/cm. The pH-measurement is also proportional to the addition in all the cases, except in deflocculant “D”, where the pH is independent of the percentage of deflocculant and it remains in a value of 8,5).

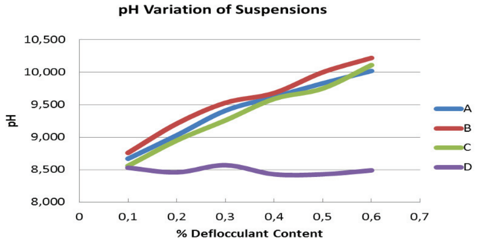

Fig. 2. Correlation between the amount of deflocculant addition and the pH of the obtained suspension.

The rheological properties of the suspensions predetermine the operational efficiency of the industrial manufacturing processes. The optimal rheological performance at low rotation rate (100 s^{-1}) was reached at 0,4% content of deflocculant “D”. This addition enables decrease of the suspension viscosity, resulting in favouring of the load/unload procedures, and increasing the efficiency of the entire production cycle (Fig. **3**a).The deflocculant additions have revealed differences at high shear rate (1000 s^{-1}) as well. The suspensions with deflocculant “B” have a wide working range from 0,2% to 0,4 %, whereas among these ones, prepared with “D” the suspension 0,4 % content revealed superior capability (Fig. 3b).

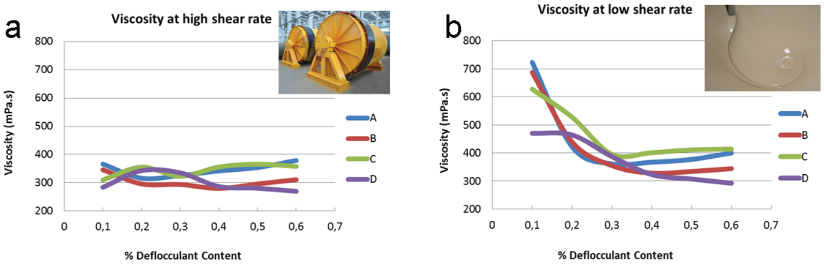

Fig. 3. Dependence between the deflocculant content and the viscosity of the obtained suspensions, determined at low-(a) and high-(b) rotation rates.

Comparison of the impact of the deflocculant addition on the thixotropy was performed, as well. The measurements have shown that the deflocculant ”D” contaning suspensions possess distinguishable behaviour. Their thixotropy continuously decreased with increase of the addition content, whereas for all the rest deflocculants a minimum was observed.

CONCLUSION

The present research has compared the rheological effect of different mechanisms of defloculation on a porcelain ceramic paste. Deflocculant “D” with complexant action presents the lowest pH and the highest conductivity, while the rest of deflocculants characterized by their silicated composition have a similar pH. Because of that, suspensions containing deflocculant “D” present lower pH.

Deflocculant “D” is the best to get an optimum viscosity during the industrial ball mill process, in which the shear rate is low. At high shear rates, during the ceramic spray drying process, deflocculant “B” (charges and steric effect) presents the lowest viscosity around 0,2%-0,4% content deflocculant, whereas deflocculant “D” tends to decrease viscosity from 0,4% to higher percentages of addition. The lowest thixotropy is shown by deflocculant “D”, while the others ones present a narrower range of rheological stability.

In conclusion, the four tested deflocculants can be used to stabilize ceramic porcelain pastes, although the complexant mechanism is the more suitable to reduce viscosity and thixotropy.

Acknowledgements: We thank to Zschimmer & Schwarz - España S.A. for the technological advice and the supply of the four deflocculants tested in this research.

REFERENCES

[1] Monfort E., A. Mezquita, G. Mallol, R. Granel, E. Vaque, “Guía de ahorro energético en el sector de baldosas cerámicas de la Comunidad Valenciana”, Agencia Valenciana de la Energía, 2008.

[2] Monfort E., A. Mezquita, G. Mallol, R. Granel, E. Vaquer, “Estudio energético del sector de baldosas cerámicas de la Comunidad Valenciana”, Agencia Valenciana de la Energía, 2011.

[3] Portillo C., “Reología de materiales cerámicos.” [Online]. Available: http://www.bubok.es/libros/210038/REOLOGIA-DE-MATERIALES-CERAMICOS. [Accessed: 14-Oct-2014].

[4] Ayadi A. J., J. Soro, A. Kamoun, S. Baklouti, R. D. S. Sfax, A. A. Thomas, “Study of clay´s mineralogy effect on rheological behaviour of ceramic suspensions using an experimental design”, International Journal of Research and Reviews in Applied Sciences, 14, 2013, 374–384.

[5] Neto J. B., A. P. Novaes de Oliveira, O. E. Alarcon, P. Pozzi, F. Andreola, “Comparative study of deflocculation mechanisms in colloidal clay suspensions”, VII World Congress on Ceramic Tile Quality, Castellón (Spain) 2002, pp. P. G-1 283 - 300.

[6] Zschimmer and Schwarz GmbH & CoKG, “Mechanisms of action of deflocculants and dispersants in ceramic bodies”, access via: http://www.zschimmerschwarz.com/en/simon/zschimmerschwarz/media/site/downloads/fachinfo/eng/Fach/E_WirkmechVerfluess.pdf.

[7] Papo A., L. Piani, “Rheological Properties of Alumina Slurries: Effect of Deflocculant Addition”, Part. Sci. Technol., 25, (4), ,2007, 375–380.

[8] Xiaoran L. H., “Study on the Preparation and Properties of a New Type Composite Deflocculant of Ceramic,” Ceramics, 2007.

[9] Schramm G., “A Practical Approach to Rheology and Rheometry”, 2nd Ed. Gebrueder HAAKE GmbH, Karlsruhe (Germany - 1994), 15 - 17.

About the authors

Dr. Ester Barrachina Albert, Department of Inorganic and Organic Chemistry. Universitat Jaume I of Castellón (Spain). E-mail: ebarrach@uji.es

This paper has been reviewed