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Mixture design to optimize the amount of deflocculants in aqueous porcelain precursor suspensions

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The performance of dispersants poly(acrylic acid), a poly(methacrylic acid), sodium silicate, as well as binary and ternary deflocculant mixtures was compared for highly concentrated aqueous porcelain suspensions. These were formulated in ten stoneware recipes which were processed in the laboratory under fixed conditions, similar to those used in the ceramics industry, and viscosity measurements were made. The use of this methodology enabled the calculation of valid regression models (equations) relating viscosity with the contents of different deflocculant mixtures.

Key words: Porcelain, Rheology, Thixotropy, Mixture design.

Introduction

The rheological stability of a slip is one of the most important properties necessary for the production of uniformly high quality materials [1]. When ceramic powders are added to a suspending medium such as water, the presence of attractive van der Waals forces typically results in the particles aggregating to form clusters. These flocculated suspensions display a relatively high-suspension viscosity that can make processing difficult and, more importantly, the flocs can become flaws in the final microstructure leading to a reduction in the final component properties. By this, efficient de-agglomeration and dispersion of the ceramic powder in a liquid medium is crucial for minimizing defects. To obtain a ceramic suspension with high solids content that can be successfully processed it is necessary to have a low viscosity and stability. This requires efficient dispersants and conditions to obtain components with high green strength, which facilitates early mould release and green machining.

Silicate and polyacrylate sodium salts are the most common chemical additives in the production of tiles, dinnerware, sanitaryware and whiteware. They are commercially available products with good deflocculant abilities and performance-to-cost ratios. Sodium silicate is widely used in the ceramic industry because of its low cost and suitable deflocculant effect, which occurs, mainly, by electrostatic stabilization. The deflocculating ability of sodium silicate ($Na_2O{\cdot}nSiO_2$) salts is due to the high colloidal protective effect (on clay particles) from the separation of colloidal SiO_2 [2] and removes flocculating cations by the combination of these with silicate ions [3]. Sodium polyacrilate and the sodium polymethacrilate are linear polymers and anionic polyelectrolytes, thus the stabilization of the suspensions are essentially derived from two combined effects: the electrostatic and the steric mechanisms. Steric repulsion is believed to play an important role in the stabilization of systems with high solids loadings. In sterically-stabilized systems the flocculation is prevented since the total energy interaction is repulsive also at very short distances provided that the surfaces are completely covered with polymer. The steric repulsion originates from free energy changes due to interactions between adsorbed polymer chains as the particles are brought together [4].

Despite the extensive research in the area of water-based ceramic processing, few studies compare in a systematic way the function of dispersants as the interaction alone and between them with the solids due to the different stabilizing mechanisms in aqueous ceramic suspensions at high solids loadings. The aim of the present study has been to evaluate the efficiency of three dispersants with different stabilizing mechanisms in dispersing mixtures of clays at high solids loadings, using a mixture design with central points as a statistical approach.

Experimental

A porcelain stoneware slip was prepared using industrial raw materials and a typical mix composition, the chemical composition, density, particle size and superficial area are shown in Table 1, these being kaolin EPK, nepheline syenite A270, silica mesh 208 and ball clay OM4 all of them given by the Company Industrial Ceramics in Mexico. The crystalline phases were determined by X-ray diffraction (XRD; Siemens 5000). The kaolin was present as a primary phase, the kaolinite [$Al_2Si_2O_5(OH)_4$] and the quartz as

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Table 1. Chemical composition and physical properties of the raw materials

Component	Composition (wt%)			
	Kaolin EPK	Ball Clay OM4	Nepheline	Quartz
SiO_2	45.3	44.70	61.00	100
Al_2O_3	38.38	38.30	23.40	0
Fe_2O_3	0.30	0.60	0.00	0
TiO_2	1.44	2.40	0.00	0
MgO	0.25	0.10	0.01	0
CaO	0.05	0.10	0.25	0
Na_2O	0.27	0.10	9.80	0
K_20	0.04	0.10	4.50	0
LOI (950)	13.97	13.60	1.04	0
Density(g/cm^3)	2.6187	2.5517	3.5754	2.6651
Media particle size (μm)	1.43	1.36	2.41	5.92
Specific superficial area (m^2/g)	24	22	1.1	0.9

secondaries. The nepheline syenite contains primarily albite and nepheline syanite. The clay consists of kaolinite and quartz and the silica it contains is almost in its entirety the quartz phase. The densities of each one of the materials were determined by a gas pycnometer ACCUPYC 1330. The particle size distribution of the raw materials was determined by a photosedimentation technique, using a Horiba CAPA 300. The specific surface area was determined by Brunauer-Emmett-Teller method (Quantasorb Jr.)

The deflocculants used were sodium silicate with a relationship of silica/soda 1 : 3, poly(methacrylic acid) with specific density of 1.17 and poly(acrylic acid) with density of 1.3.

The suspensions were prepared with distilled water adding the clays first and later on the rest of the components (as commonly it is made in industry) by mechanical mixing. 25×10^{-3} m^3 of the porcelain batch were initially prepared at 45 vol% of solids without any dispersants. To introduce the deflocculants, the suspension was divided in four parts, three portions of 5×10^{-3} m^3 and one of 10×10^{-3} m^3, once divided, the specific gravity were adjusted to 1.7 (40 vol% of solids). The suspension of 10×10^{-3} m^3 had no dispersant added while to the other three were added 1 wt% of poly (acrylic acid) (Darvan 811), 3.5 wt% of sodium silcate and 1 wt% of poly(methacrylic acid) (Darvan 7), respectively, in the water solution. For example to obtain a concentration of 0.10 wt% (in the case of the Darvan7) 90 ml of the suspension was mixed without any deflocculant with 10 ml of the suspension that contains a concentration of 1.0 wt%, all the mixtures for each one of the deflocculants were prepared in this way.

All the samples were stored for three weeks in sealed polypropylene bottles prior to testing with the purpose of eliminating the factor of aging as a variable to consider.

The viscosity of the concentrated suspensions were studied using a rotational viscometer (Brookfield Viscometer Model DV-I+) with a coaxial cylinder geometry in isothermal conditions (20 ºC).

Table 2. Mixture compositions and corresponding measured values of viscosity

Design Mixture	Weight fractions			Viscosity (cP)
	Darvan 7	Darvan 811	$Na_2O.nSiO_2$	
1	1.000	0.000	0.000	320
2	0.000	1.000	0.000	144
3	0.000	0.000	1.000	155
4	0.500	0.500	0.000	145
5	0.500	0.000	0.500	148
6	0.000	0.500	0.500	108
7	0.667	0.167	0.167	185
8	0.167	0.667	0.167	120
9	0.167	0.167	0.667	195
10	0.333	0.333	0.333	143

The optimum amount of each one of the defloculants was the experimental point that corresponds to the lowest value of the apparent viscosity. A {3,2} centroid simplex -lattice design, augmented with

interior points, was used to define the mixtures of these defloculants that should be investigated. The selected mixture was done using the optimum defloculant in the percent that was indicated by the design. The apparent viscosities were read and from these values were calculated the coefficients of the regression equation which represented a model that related the viscosity with the mixture of deflocculants. All the calculations were conducted using STATISTICA (StafSoft, 2000).

Results and Discussion

All the slurries tested are non-Newtonian systems. They exhibit a pseduoplastic nonlinear behavior. Having a measured value for the property response at specific coordinates (Table 2), a regression equation can be sought for the property. Linear, second and third degree regressions were evaluated, subjected to a significance level of 5%. Tables 3 give the various statistical properties of the regressions for viscosity, using the nomenclature commonly found in the relevant texts [5, 6].

Using the p-value approach to hypothesis testing (*i.e.* p value ≤ significance level), Table 3 show that the linear model does not reach the stipulated significance value. The second, special third and full third degree models are statistically significant at that level in the case of linear, quadratic and special cubic models the corresponding coefficients of multiple determinations, R^2, show that the models present small variability, but in the cubic model the variability is smaller than the other models. Table 4 shows the coefficients of the factors of the cubic model, if we make a t-test and compare the t calculated versus the t tabulate as it appear in Fig. 1 we can get the final equation, relating the viscosity with the proportions of the independent components:

Table 3. Variance Analysis for significance of the regression models for viscosity*

	SS	df	MS	SSE	MS	F	R^2	R^2_A
Linear	38477.56	2	19238.78	26114.64	1536.156	12.52398	0.596	0.548
Quadratic	16660.32	3	5553.44	9454.33	675.309	8.22355	0.854	0.801
Special Cubic	2631.37	1	2631.37	6822.95	524.842	5.01365	0.894	0.846
Cubic	5987.03	2	2993.52	835.92	75.993	39.39205	0.987	0.978
Total Adjusted	64592.20	19	3399.59					

* SS: Sum of squares; df: freedom degrees; MS: Mean squares; SSE: error sum of squares; F: F test; R^2: coefficient of multiple determination; R^2_A: adjusted R^2.

Table 4. Coefficient factors of the cubic model

	Coeff.	Std.Err.	t(11)
(A)Darvan7	321.431	6.1490	52.2738
(B)Darvan 811	145.431	6.1490	23.6512
(C)$Na_2O.nSiO_2$	156.431	6.1490	25.4401
AB	-342.275	30.1485	-11.3529
AC	-352.275	30.1485	-11.6846
BC	-160.275	30.1485	-5.3162
ABC	1163.647	197.7499	5.8844
AB(A-B)	380.000	100.1552	3.7941
AC(A-C)	886.000	100.1552	-8.8463

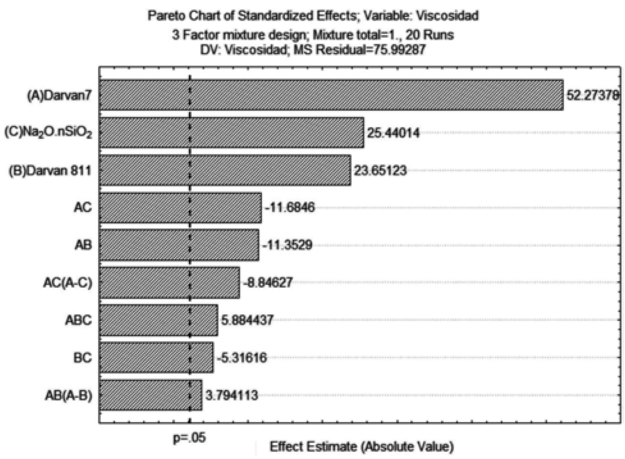

Fig. 1. Pareto chart of standardized effects.

$$\text{Viscosity} = 321.41A + 145..431B + 156.431C - 342.275AB - 352.275AC - 160.275BC + 1163.647BC + 380.000AB(A\text{-}B) - 886.000AC(A\text{-}C). \quad (1)$$

Where A, B and C are the defloculator fractions of Darvan 7, Darvan 811 and sodium silicate, respectively.

The fact that the models obtained are statistically significant at the specified level does not mean that they are valid. Fig. 2 is a plot of the viscosity raw residuals (*i.e.* difference between the experimentally-determined value and the calculated estimate) as a function of the predicted viscosity values, and shows that the errors can be considered randomly distributed around a zero mean value, hence are uncorrelated, which suggests a common constant variance for all the viscosity values. Fig. 3 shows that a straight line can be considered to relate the residuals with the expected

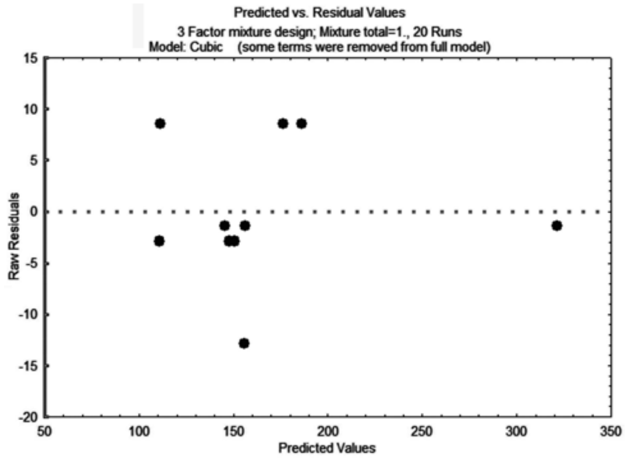

Fig. 2. Viscosity residual analysis Raw residuals vs. Predicted values.

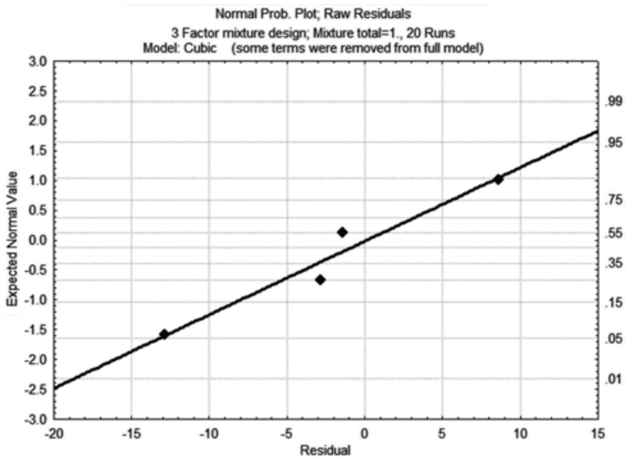

Fig. 3. Normal probability curve.

normal values, meaning that the distribution is normal [7, 8]. Thus, the experimental model can be considered adequate and a good estimate of the viscosity can be obtained using Eq. (1).

Fig. 4 shows the projection of the calculated response surface onto the composition triangle; it can be seen from Fig. 4 that the binary mixture allows a better rheological behavior than the single additives, the mixtures permit a reduction of the apparent viscosity of the slurries with respect to those prepared using only one deflocculant. In fact, all the binary mixtures prepared presented the best performance,

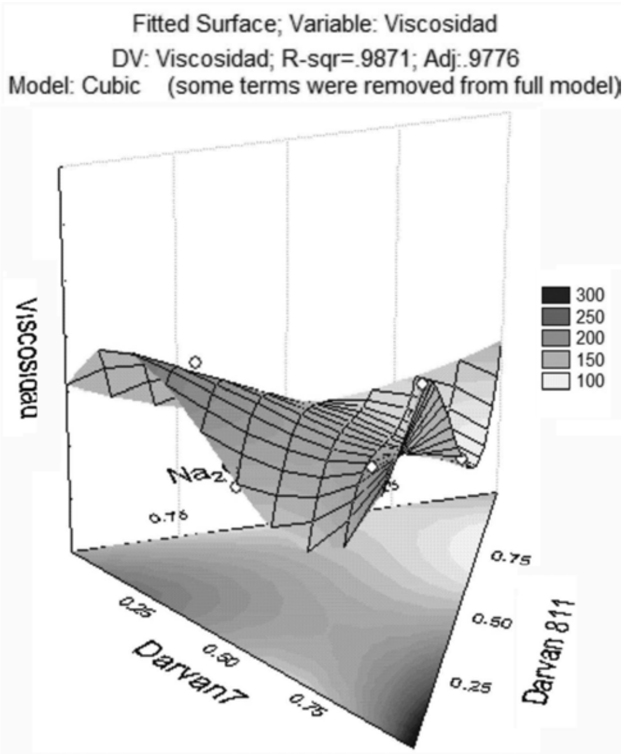

Fig. 4. Variation of viscosity as a function of coded variables.

reducing the apparent viscosity. Ternary mixtures permit maintenance of the characteristics observed in the binary mixtures.

Conclusions

The use of deflocculant mixtures in the traditional ceramics field allows better deflocculation conditions compared to the single additives. Binary and ternary mixtures allow a reduction of the apparent viscosity with respect to slurries prepared using each additive alone.

The use of experimental design and the use of methods to change the surface response, allowed elaborating statistical experimental models that correlate the mixtures of deflocculant with the apparent viscosity of the suspensions with a regression of 98 %, allowing to control a more efficient way for the process of slip casting.

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