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Mixture of deflocculants: A systematic approach

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Abstract

In the production of ceramic tiles, during wet grinding, chemical additives are normally used to increase the solid loading of the suspensions. Commonly, mixtures of organic and inorganic chemical additives are used to reduce viscosity and costs. In literature, only few papers consider the combined effect of two or more deflocculants and a modest knowledge has developed on possible competitive or synergic interactions among them. The most common rheological additives show different behaviour depending on the clay. With mixture design it is possible to define mathematical models by means of which it is possible to engineer the rheological behaviour of a suspension.

Keywords: Rheology; Suspensions; Traditional ceramics; Mixing

1. Introduction

In the production of ceramic tiles, the raw materials and the components of the glazes are reduced in size and homogenised by milling. Aqueous, continuous or discontinuous wet milling are the most used techniques. The solid loading of the suspensions is about 63–67% by weight in industrial water. To reduce their viscosity, chemical additives are normally utilised. In ceramic tile industry, inorganic substances (as silicates, phosphates and carbonates sodium salts) or organic additives, generally polyacrylates salts with different molecular structures, are commonly used. They are added in a percentage between 0.1% and 0.6% by weight, to reduce the viscosity under 1 Pa s, typically around 200–400 mPa s. The mechanism of sodium silicate consists in a variation of the pH of the suspension and a specific adsorption of the negatively charged deflocculant anions on the clay positive edges, being the driving force of electrostatic nature.[1] In the market, silicates are available with different ratio Na_2O/SiO_2; in the industrial practice are commonly used the ratios between 1:1 and 1:2. The phosphates with more remarkable deflocculant effectiveness are sodium hexametaphosphate $(NaPO_3)_6$ and sodium tripolyphosphate ($Na_5P_3O_{10}$). The phosphate anion is adsorbed onto clay particle edges, increasing their negative charge. Moreover, polyphosphate decreases the concentrations of flocculant bivalent cations through their complexation performed by not adsorbed deflocculant molecules.[2] Polyacrylates, sodium or ammonium salts, are deflocculants with high efficiency. Their anions are easily adsorbed on the clay particles increasing the negative charge and determining an electrosteric repulsion.[3] In literature, only few papers consider the combined effect of two or more deflocculants in the suspension while, in the industrial production this is usual practice.[4] In this way, the apparent viscosity responses and the time-dependent behaviour observed using the most efficient deflocculant might be obtained with an appropriate mixture, but at lower cost. A deeper knowledge about the mutual interaction between the additives can allow an optimisation of the ceramic process. Differently from the most used approach "try and error", the statistical method of mixture design, a part the design of experiments (DOE), can be used to study the influences of two or more additives. It is a structured and organized method for determining the relationship between the components and the output of that process. A correct experimental planning permits to get more information with a lower effort and reduces the subjectivity of the results increasing their technical and scientific values. It generates a map of the response over a specified region of formulation. It is possible to discover the critical variables, to define mathematical models and, by them, to optimise the product and the industrial process.[5,6] In the present work, the effectiveness of three of the most used deflocculants in tile ceramic production with respect to three typical clays is taken into consideration and defined by mathematical models. These last ones are then used to engineer the rheology of suspensions.

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2. Experimental

The systems studied were raw materials used in the industrial production of tiles: a kaolinitic, an illitic-kaolinitic and an illitic-chloritic clay. The additives used were: an anhydrous sodium metasilicate NaSil (Solvay-ex Ausimont); a sodium tripolyphosphate NaTPP (Smaltochimica S.p.A.); a sodium polyacrylate NaPol (Lamberti S.p.A.). The mixtures of deflocculant were prepared according to the scheme in Fig. 1. It is a simplex-centroid mixture design augmented with four replications introduced to get a measure of error. The run order for experiments was randomised to counteract any time-related effects. For each clay, the suspensions were prepared in a fast ball mill for 20 min as shown in Table 1. Viscosity was measured at room temperature using a Haake CV20 Rheometer with concentric cylinder geometry. The measure procedure used is shown in Fig. 2. The first part, step I and II, has the purpose to give to all the samples the same rheological history. The data at 50–100 and 200 s^{-1} were obtained in step III and analysed using Design-Expert v. 6.0.10 by Stat-ease Inc.

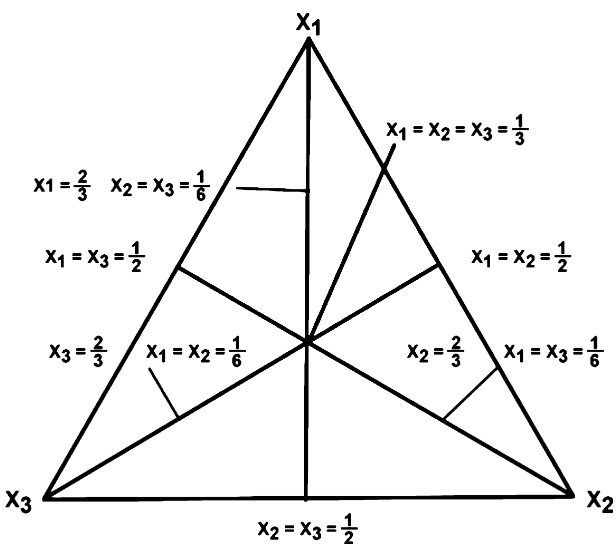

Fig. 1. Mixture design used: simplex-centroid mixture design augmented.

Table 1
Composition of suspensions

	Kaolinitic clay (wt.%)	Illitic-kaolinitic clay (wt.%)	Illitic-chloritic clay (wt.%)
Solid loading (%)	67	70	55
Water loading (%)	33	30	45
Deflocculant (% dry matter active principle)	0.3	0.3	0.3

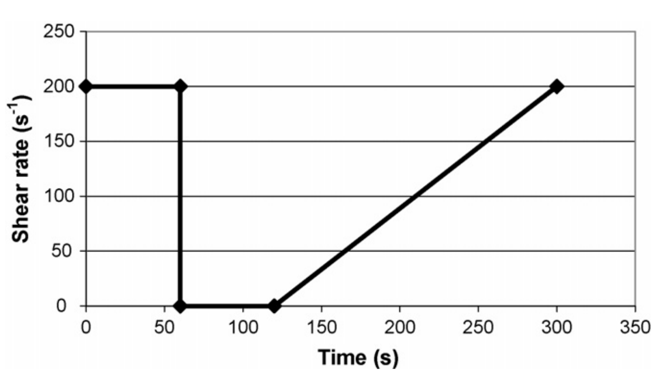

Fig. 2. Measure procedure used to determine the rheological behaviour of the systems.

3. Results and discussion

3.1. Kaolinitic clay

The observed rheological behaviour for kaolinitic clay is the well-know shear thinning with low yield point. In Fig. 3 the 3D plot of viscosity at 50 s^{-1} versus composition of the mixture is presented. The plots at higher shear rates are qualitatively similar to this one. The NaSil is less efficient between the three chemical substances, as it is shown in Eqs. (1)–(3), where the viscosities at three different shear rates are correlated with the percentage of the three deflocculants in the mixture. The coefficient of silicate is higher than the coefficients of NaPol and NaTPP. On the contrary, all the other coefficients relative to the combinations of two chemical additives are negatives. It means that interactions are present and produce a reduction of viscosity. NaTPP shows the best efficiency and the NaPol is set very close to the phosphate, but at values slightly higher. The difference is confirmed also considering the 95% confidence level:

$$\eta_{50\,\mathrm{s}^{-1}}^{0.38} = 3.33\mathrm{P} + 2.27\mathrm{F} + 4.25\mathrm{S} - 4.62\mathrm{PF} - 25.79\mathrm{PS} - 15.87\mathrm{FS} - 111.06\mathrm{PF}(\mathrm{P} - \mathrm{F}) \quad (1)$$

$$\sqrt{\eta_{100\,\mathrm{s}^{-1}}} = 2.79\mathrm{P} + 1.71\mathrm{F} + 3.40\mathrm{S} - 2.27\mathrm{PF} - 24.02\mathrm{PS} - 14.81\mathrm{FS} - 88.98\mathrm{PF}(\mathrm{P} - \mathrm{F}) \quad (2)$$

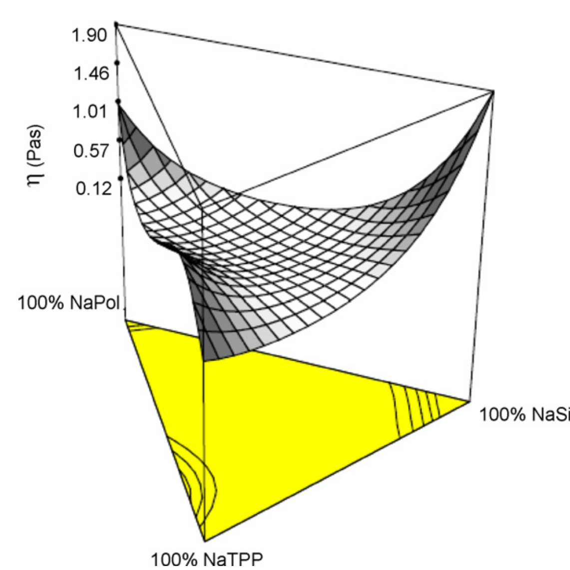

Fig. 3. Kaolinitic clay viscosity at $\dot{\gamma} = 50\,\mathrm{s}^{-1}$.

$$\eta_{200\,\mathrm{s}^{-1}}^{0.22} = 2.80\mathrm{P} + 2.35\mathrm{F} + 3.02\mathrm{S} - 0.81\mathrm{PF} - 11.17\mathrm{PS} - 7.13\mathrm{FS} - 37.09\mathrm{PF(P-F)} \quad (3)$$

where P is the NaPolyacrylate (wt.%), F the NaTPP (wt.%) and S is the NaSil (wt.%).

The binary mixtures between NaSil–NaTPP, NaSil–NaPol and NaPol–NaTPP show synergic interactions. In the first case, the viscosity decreases up to reach a minimum for the mixture with 0.16% of NaTPP and 0.14% of NaSil. In the second case, the minimum is obtained with the 0.18% of NaSil and the 0.12% of NaPol. Between NaTPP and NaPol, the minimum is reached with the 0.30% of NaTPP, but also the mixture formed by the 0.18% of NaPol shows values of very low viscosity. The minimum for the whole simplex is reached with a ternary mixture: 0.10% of NaPol, 0.04% of NaTPP and 0.16% of NaSil.

3.2. Illitic-kaolinitic clay

The deflocculants show a different effect on the rheology of the illitic-kaolinitic clay with respect to the kaolinitic clay, as it is observable in Fig. 4 and Eqs. (4)–(6). In general, for all the samples, the rheological behaviour is shear thinning with low yield point. Sodium SIL and sodium TPP permit to obtain the same value of viscosity both at 50 and 100 s^{-1}, while at 200 s^{-1} the phosphate is more efficient. Sodium polyacrylate is the deflocculant with the worst performance. Its effect is clear from 0.23% to 0.3%. In this interval, the viscosity grows up to the maximum. In general the interactions among the additives are not important:

$$\eta_{50\,\mathrm{s}^{-1}} = 10^{2.16\mathrm{P}-2.12\mathrm{F}-0.72\mathrm{S}-25.25\mathrm{PF}-45.50\mathrm{PS}-9.48\mathrm{FS}-76.43\mathrm{PF(P-F)}-87.96\mathrm{PS(P-S)}} \quad (4)$$

$$\eta_{100\,\mathrm{s}^{-1}}^{-0.24} = 2.65\mathrm{P} + 5.03\mathrm{F} + 4.04\mathrm{S} + 12.92\mathrm{PF} + 26.68\mathrm{PS} + 5.46\mathrm{FS} + 29.96\mathrm{PF(P-F)} + 43.57\mathrm{PS(P-S)} \quad (5)$$

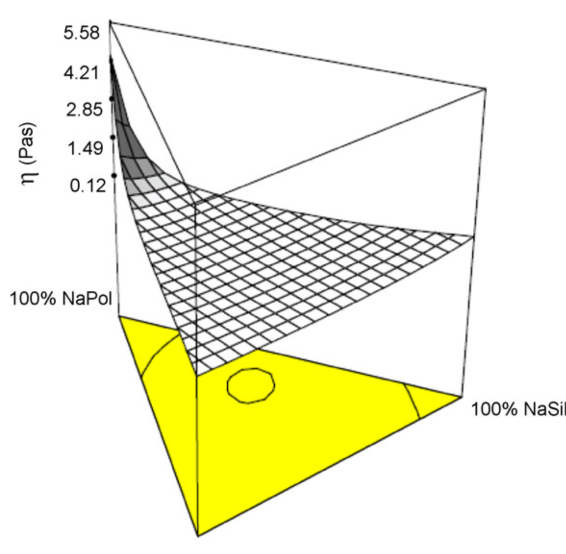

Fig. 4. Illitic-kaolinitic clay viscosity at $\dot{\gamma} = 50\,\mathrm{s}^{-1}$.

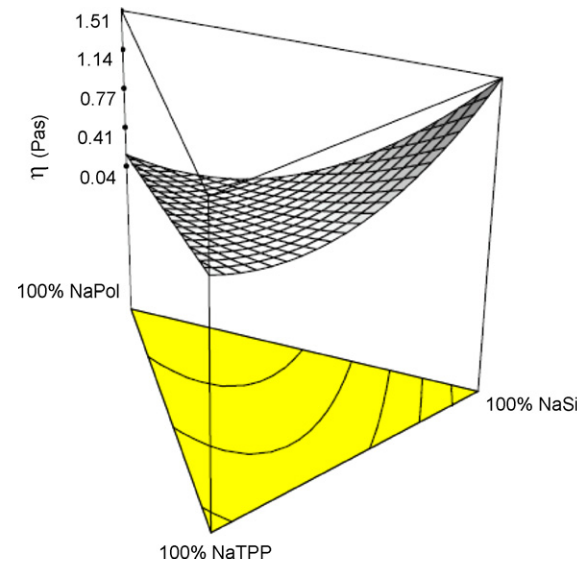

Fig. 5. Illitic-chloritic clay viscosity at $\dot{\gamma} = 50\,\mathrm{s}^{-1}$.

$$\eta_{200\,\mathrm{s}^{-1}}^{-1.64} = 28.52\mathrm{P} + 82.64\mathrm{F} + 22.74\mathrm{S} + 1054.35\mathrm{PS} \quad (6)$$

3.3. Illitic-chloritic clay

The rheological behaviour of the suspension with the illitic-chloritic clay is again shear thinning at all the values of shear rates with low yield point. However, it shows a better sensitivity to the action of the NaPol, as it is evident in Fig. 5 and Eqs. (7)–(9):

$$\eta_{50\,\mathrm{s}^{-1}} = 0.51\mathrm{P} + 2.91\mathrm{F} + 5.04\mathrm{S} - 23.10\mathrm{PS} - 19.68\mathrm{FS} \quad (7)$$

$$\eta_{100\,\mathrm{s}^{-1}}^{1.29} = 0.32\mathrm{P} + 1.48\mathrm{F} + 2.93\mathrm{S} - 13.22\mathrm{PS} - 12.27\mathrm{FS} \quad (8)$$

$$\eta_{200\,\mathrm{s}^{-1}} = 0.35\mathrm{P} + 1.24\mathrm{F} + 1.69\mathrm{S} - 6.02\mathrm{FS} \quad (9)$$

Silicate shows the worst efficiency while the effect of NaTPP is places between these two substances. Interactions are present and synergical effects are observable in the mixtures of NaPol–NaSil and NaTPP–NaSil. The lowest value of viscosity is obtainable with pure NaPol.

3.4. The models

The systematic approach used allows to understand the effect of the select additives on mineralogical different clays and also to define in a quantitative way the effects of interactions among the deflocculant. From a practical point of view, it furnishes the necessary elements to optimise the process of milling and reducing the cost of spray-drying. A further advantage is the availability of a quantitative model to realize a rheological behaviour only imagined in the mind. In other words it is possible to engineer the rheology of a suspension working on the composition of the deflocculant. That it is of great importance in industrial

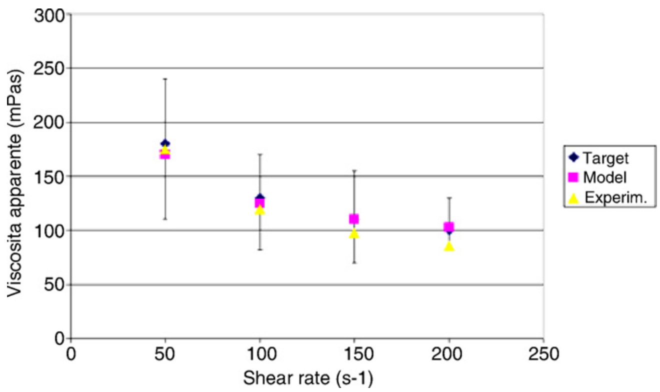

Fig. 6. Results of the test carried out on model for kaolinitic clay (⧫). Wished rheological behaviour, (■) closest rheological behaviour obtainable using the model (▲) rheological behaviour obtainable experimentally using the model.

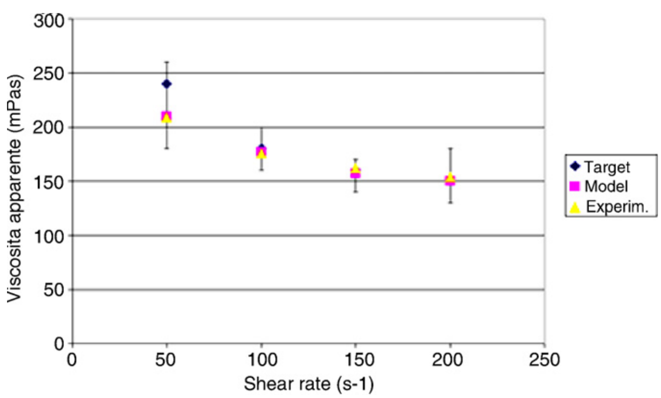

Fig. 7. Results of the test carried out on model for illitic-kaolinitic clay (⧫). Wished rheological behaviour, (■) closest rheological behaviour obtainable using the model (▲) rheological behaviour obtainable experimentally using the model.

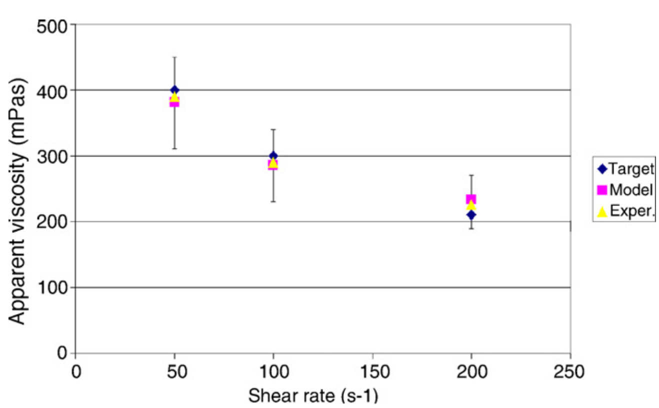

Fig. 8. Results of the test carried out on model for illitic-chloritic clay (⧫). Wished rheological behaviour, (■) closest rheological behaviour obtainable using the model (▲) rheological behaviour obtainable experimentally using the model.

applications because permits to achieve in a fast way the wished rheological behaviour. In Figs. 6–8 the results of a tests with the three clays are shown. The wished rheological curve (⧫) and the best curve obtainable using the models optimisation algorithms (■) are close, also if the confidence interval bars are not considered. The experimental results (▲), obtained on the suspension prepared using the mixture of deflocculant suggested by the models is nevertheless close to the wished curve. Also in the case of Fig. 7, the overlapping among experimental, calculated and the wished curve is excellent, with the exception of the viscosity at 50 s^{-1} where the difference is more significant, even if inside the confidence interval. The result of optimisation depends by a number of reasons. The first of all is the more trivial: the experimenter could have carried out the experiment with superficiality, making mistakes. The results are incorrect for incompetence of the experimenter, not due to the method. The second reason can be due to the error/variability of the measures. Also in this case the failure is ascribable not to the method but to the inevitable error connected with measure. A third class of difference is imputable to the choice of the points that to shape the desiderated curve. In fact, it is not always possible to determine a mix of deflocculants able to fit perfectly the values of the desiderated curve. Moreover the results of the algorithms of optimisation depend, as in the present case, by the weights that we attribute to one or more goals.

4. Conclusions

Mixture design was used with success for the study of organic and inorganic deflocculants. It has permitted to define models that describe the efficiency of the chemical additives pure or in mixture. Synergical interactions were highlighted as a function of the clay family. Algorithms of optimisation permit to engineer the rheology of a suspension, with the limit implicit in any method.

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