RHEOLOGICAL BEHAVIOUR OF GLAZE SUSPENSIONS. INFLUENCE OF FRIT SOLUBILITY, PH, WATER HARDNESS AND ADDITIVES

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ABSTRACT

To obtain high quality glazed tile, the rheological behaviour of the glaze suspensions used must be appropriate, since the correct application of the suspension to the ceramic body, the characteristics of the unfired glaze layer, and to a large extent the characteristics of the resulting final fired glaze coating as well, all depend on the glaze suspension's rheological behaviour.

The study has allowed determining how different factors affect the rheological behaviour (yield stress and viscosity) of the glaze slips employed in fabricating porous wall tile. The studied factors were: frit solubility, pH, hardness of the water used, and the nature and proportion of the various additives usually included in this kind of suspension (binder, deflocculant, and NaCl).

An experimental relation has been established between frit solubility (solubilized sodium/potassium concentrations ratio), and the yield stress of the resulting glaze suspensions. In order to obtain this relation, it was necessary to prepare an experimental method for determining the cations solubilized by the frit during milling, as well as carrying out tests using a considerable number of frits with differing compositions.

Finally, a relationship could be established between the variations arising in yield stress and the changes in the properties of the unfired glaze layer (surface drying time), which confirmed the validity of this rheological parameter for assessing how a suspension will behave in the glazing operation.

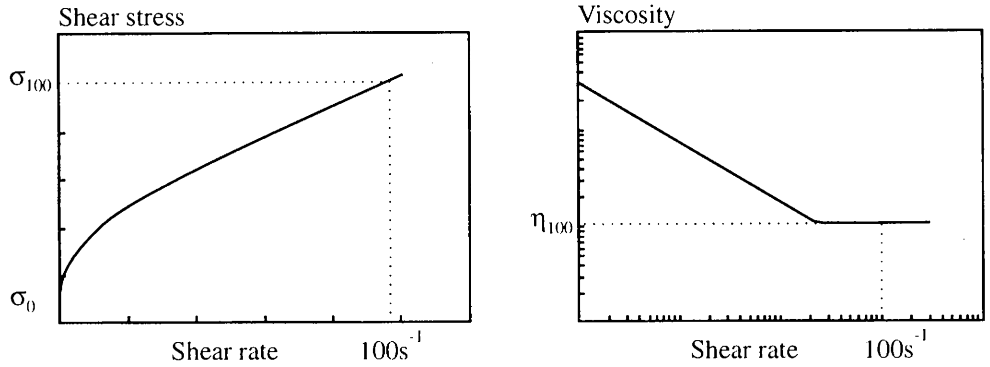
The findings indicate that the determination of frit solubility and the use of the appropriate additives allow obtaining glaze suspensions with the required rheological behaviour for the subsequent glazing process.

1. INTRODUCTION

In glazed ceramic tile manufacturing processes, the most widespread glazing method is that of bell glazing. This technique yields quite thick layers of glaze that exhibit a good surface texture [1][2].

The glaze suspensions that are applied by this procedure must have suitable rheological behaviour in order to produce glazed tile without any faults arising as a result of the glazing operation (uneven surfaces, lumps, pinholing, cracks, etc.)[3][4]. Moreover, the rheological characteristics of these suspensions also affect the properties of the layer that is formed (porosity, permeability, consistency, etc.)[5], therefore impacting the properties of the resulting final glaze coating.

These suspensions are usually characterized by the rheological behaviour illustrated in Fig. 1 [6-9]. It can be defined by using the experimental parameters: yield stress (σ_0) and viscosity at a given shear rate. In this study, the viscosity value at a shear rate of 100 s^{-1} (η_{100}) was used.



a) b)

Figure 1. a) Flow curve and b) Variation of viscosity with the shear rate for a glaze suspension applied by bell glazing.

The value of the yield stress is largely determined by the presence of agglomerates in the suspension. Their presence raises σ_0 and viscosity at low shear rates, without generally affecting viscosity at high shear rates. This is because when the suspension is subjected to flow, the existing agglomerates start breaking up, until a moment comes (high shear rates) at which only individual particles are left [5][10].

The suspensions containing large amounts of agglomerates (high σ_0 values) will give rise to glaze layers with a more open structure, characterized by: low bulk density and mechanical strength, easy elimination of the water existing between the agglomerates, high moisture content in the consolidated layer, and high drying shrinkage. On the other hand, in this type of suspension, the air bubbles that may be present within the glaze will be hard to remove, and they will give rise to voluminous sediments that are readily redispersible [5][11].

However, when glaze suspensions contain few agglomerates (low σ_0 values), small volumes of compact sediments arise, which are hard to redisperse. The glaze layer that is formed from such suspensions exhibits high bulk density, with quite opposite characteristics to those of a glaze layer with a more open structure [5][11].

Agglomerates form in a suspension as a result of interparticle forces, which may be of an attractive or repulsive nature. If the resulting force is attractive, the particles tend to flocculate, whereas when repulsion prevails a dispersed or deflocculated system arises.

The resulting interparticle force will be due to the sum of all the forces that exist between the particles, which may be [12-14]:

- Attractive forces: called Van der Waals (or intermolecular) forces associated with the very nature of the particles and their size.
- Repulsive forces: produced by the electrostatic charges of the particles, caused by surface ionisation, dissolution and ion adsorption processes, or as a consequence of the presence of adsorbed polymers at the particle surface (steric repulsion).

The electrostatic charges that arise at the surface cause a charged interface to form (particle-dispersing medium), at which an electric double layer will develop as a result of the presence of surface charges that are compensated near the surface, by an unequal distribution of oppositely charged ions (counter-ions) and ions with a like charge (co-ions).

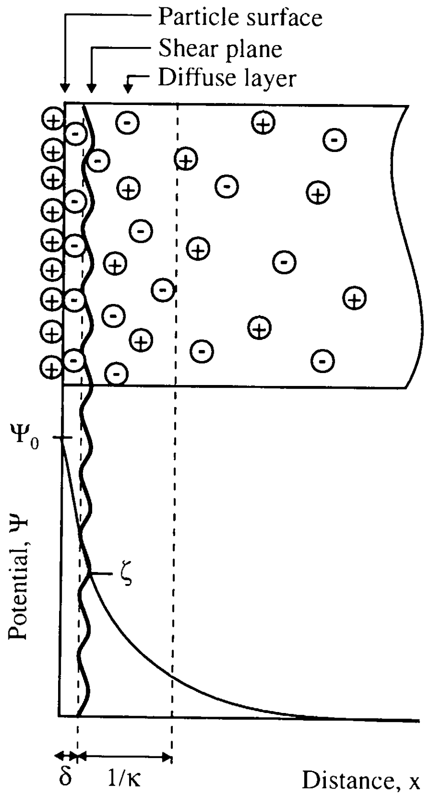


Figure 2. Structure of the electric double layer according to the Stern model.

There are different models for explaining this charge distribution, one of the currently most widely accepted ones being the Stern model[12][13]. According to this model, the ions in the solution can be specifically adsorbed at the particle surface. In this process, there is a preferential tendency for counter-ion adsorption rather than co-ion adsorption to take place at the particle surface, producing a situation like the one depicted in Fig. 2. The thickness δ will be a function of the size of the adsorbed counter-ions at the particle surface. The thickness of the diffuse layer $(1/\kappa)$ will depend on the quantity and type of ions present in this region, as κ is directly proportional to the square root of the medium's ionic force. The potential in the shear plane (called ς (zeta) potential) will be determined by the kind of ions present in the double layer, as well as by the ion adsorption density at the particle surface.

When the double layer surrounding the particles starts overlapping, repulsion arises, which is determined by the extension of this double layer. If such repulsion exceeds the Van der Waals attraction forces, a dispersed suspension forms. On the other hand, if the repulsive forces are not strong enough, the Van der Waals attraction forces prevail, and aggregation or flocculation of the suspension occurs.

The use of agents that are adsorbed and bear the same electric charge as the particle surface will enhance repulsion as a result of the electric double layer. The adsorbed additive produces a shift in the shear plane towards a region that is further away from the particle surface (steric hindrance), which increases the repulsion interval of the electric double layer.

In a glaze suspension of the kind usually employed in wall tile manufacture, the major solids fraction consists of frit particles (90-95% by weight), while the remaining solids are usually kaolin particles.

Due to their plate-like structure, the kaolin particles contained in the suspension have two regions with different electrostatic charges, namely their faces and edges, while the magnitude and sign of the charge depend on pH [15-19]. Generally, for pH values exceeding 7, kaolin particles bear a net negative charge.

However, frit particles can be bearers of electrostatic charges as a result of the process of surface ionisation that any oxide undergoes in an aqueous suspension [12][13] and as a consequence of the dissolution of the glassy lattice, an extensively studied phenomenon in glasses [20-23]. Considering the similarity that exists between glasses and frits, it may be assumed that frits will be subject to the same chemical attack by water as glasses.

In a simplified manner, it may be stated that when glass comes into contact with water the following reaction takes place:

$$\equiv SiO^- M^+_{(glass)} + H_2O \Leftrightarrow \equiv Si\text{-}OH_{(glass)} + M^+ + OH^- \qquad (1)$$

This produces a rise in the pH of the water. If the water is not changed, pH increases considerably, giving rise to another attack mechanism, namely, alkali attack (pH>9). When this happens, the silica lattice starts breaking down according to the reaction:

$$\begin{matrix} \equiv Si\text{-}O\text{-}Si\equiv_{(glass)} \\ \equiv Si\text{-}O\text{-}M\text{-}O\text{-}Si\equiv_{(glass)} \end{matrix} + (1+n)OH^- \Leftrightarrow \equiv Si\text{-}OH_{(glass)} + 3^- O\text{-}Si\equiv_{(glass)} + M(OH)_n^{2-n} \qquad (2)$$

This then gives rise to divalent lattice modifiers (M^{+2}) passing into the dissolution.

Thus, in a glaze suspension, frits can develop a surface charge that will be affected by the pH, as this parameter affects surface ionisation phenomena and frit ion dissolution. Furthermore, the ions released by the frit can modify existing interparticle forces, as a result of the phenomena described above (surface adsorption and modification of the thickness of the electric double layer).

It may therefore be inferred from the above, that the agglomeration state, and consequently the rheological behaviour of a suspension, will depend upon several factors, such as:

- pH, as this affects the particle surface charge and ion dissolution phenomena.
- The presence of different ions proceeding from frit dissolution, from water or from the additives used in preparing the suspension, since these ions can modify the extension of the double layer and ς potential [7][24][25].
- The presence of additives that may adsorb onto particles, such as sodium tripolyphosphate (TPF) [26-28] and sodium carboxymethylcellulose (CMC) [29-32].

The aim of this study has been to determine how the foregoing factors influence the rheological behaviour of glaze suspensions, and particularly yield stress (σ_0). The results will provide the necessary information to allow preparing suspensions with better suited rheological behaviour. It will thus be possible to reduce the flaws that arise as a result of incorrect applications, improve the properties of the unfired glaze layer, an obtain final glaze coatings with enhanced quality.

2 EXPERIMENTAL

2.1 MATERIALS

To carry out the study, nine industrially fabricated frits that yielded transparent glazes were used, five of which are employed in single-firing processes (M1, M2, M3, M4 and M5) and four in twice firing (B1, B2, B3 and B4).

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Glaze suspension preparation

Glaze suspensions were prepared from each of the nine frits, using kaolin as a suspending agent and sodium carboxymethylcellulose with an intermediate molecular weight as a binder. Both materials are commonly used in industry for obtaining glaze coatings. The frit references were also used to designate the suspensions they gave rise to (M1 to M5 and B1 to B4).

In each case, the solid matter in the suspension comprised 91 wt% frit and 9 wt% kaolin. This solid matter, together with 0.3 wt% CMC (in respect of the solid), and the distilled water required to obtain a volume fraction of 0.480 (solids content of around 71%), was milled in fast laboratory alumina ball mills until a 3 wt% oversize was obtained on a 40μm mesh screen. The reason for working with a constant volume fraction lies in the fact that the viscosity of a suspension depends on the volume of solids and not on its mass.

2.2.2 Characterization of the prepared glaze suspensions

The rheological behaviour, pH and surface drying time of the glaze layer that formed from each suspension were determined.

Rheological behaviour was determined by carrying out specific tests to obtain the flow curve and yield stress. Yield stress can also be derived from the flow curve but its value is then less accurate. Both tests were run using a concentric cylinder rotational viscometer in which the sample was thermostated at 25°C. In both cases, before proceeding with the actual determination, the sample underwent vigorous stirring for one minute, and was subsequently allowed to stand for six minutes. By so doing, any effects that might originate as a result of the material's prior history were thus suppressed.

The flow curve was obtained by controlling shear stress, which was progressively raised from zero to a maximum value that depended on the sample being tested. This flow curve was then used to obtain the viscosity value at a shear rate of 100 s^{-1} (η_{100}).

In order to find the yield stress, the sample was subjected to rising shear stress until a maximum value was reached, which was considerably lower than the shear stress applied for the determination of the flow curve, and also depended on the sample being tested. Yield stress was taken as the greatest applied shear stress before suspension viscosity decreased owing to flow.

The pH determination was carried out with a pH-meter (CRISON micropH 2001), using a suitable electrode for suspensions.

In order to determine surface drying time (t_s) of the glaze layer that formed from each respective suspension, the glaze suspensions were applied in an approximately 1.2 mm thick layer with an automatic variable-speed applicator system to a previously fired porous wall tile body. Drying time was assessed as the time that elapsed from the moment of application until the glaze layer lost its surface sheen.

Materials were used, in order to study the influence of water hardness, the sodium carboxymethylcellulose binder, the sodium tripolyphosphate deflocculant, common salt and pH, which are commonly employed for preparing these kinds of suspensions.

$CaCl_2$ was used for the calcium ion addition, and diluted solutions of HCl and NH_4OH were utilized for the pH modification, since the ions that these species contribute to the suspension (Cl^- and NH_4^+) produce a minimum reaction with the particle surface [15][16].

The addition of these materials in the various studied proportions took place prior to the milling of the glaze suspension. The milling process was carried out as set out in Section 2.2.1. The resulting suspensions were subsequently characterized by determining their rheological behaviour (σ_0 and η_{100}), pH, and in some cases surface drying time (t_s), as set out above.

2.2.3 Determination of frit solubility

A great variety of methods is available for the determination of glass solubilized ions, which differ according to the use to which the material involved is to be put [21], as solubility largely depends on temperature, the ratio of the glass specific surface area/water quantity in contact with this glass, nature of the attack (dynamic or static, acid or alkali), etc.

This was the reason for preparing a method that would enable the quantity of frit solubilized ions to be determined in the realest possible conditions.

Each of the nine frits were milled in fast laboratory alumina ball mills, jointly with the amount of distilled water needed to obey the dictate of the proportional requirement of the ratio frit quantity/water quantity indicated in Section 2.2.1. Milling continued until a 3 wt% oversize was obtained on a 40μm mesh screen.

During this operation, temperature rises, so that the resulting suspensions (frit and water) were left to cool down for 30 min. Once this time had elapsed, filtration was used to separate the solid matter from the water. Atomic absorption was then used to determine the amount of sodium, potassium, calcium and magnesium present in the resulting liquid.

The determination was repeated several times with two of the frits to be tested, and it was shown that reproducible results were obtained.

3 RESULTS

3.1 Influence of the type of frit on the rheological behaviour of glaze suspensions

Table 1 details the results of the determinations that were performed on the tested glaze suspensions (rheological behaviour, pH and surface drying time), characterized by being obtained from different frits (Section 2.2.1). The table shows that although the suspensions were prepared using the same volume fraction, with the same kind and proportion of additives, there are noticeable differences in the findings. These differences must therefore be due to the characteristics of the frits used.

Table 1. *Rheological behaviour (σ_0 and η_{100}), pH and surface drying time (t_s) of the glaze suspensions prepared using the nine tested frits.*

Suspensión	σ_0 (Pa)	η_{100} (Pa.s)	pH	t_s (s)
M1	3.9	1.621	10.2	45
M2	5.7	1.300	10.3	37
M3	8.6	1.426	10.0	36
M4	6.2	1.436	9.8	36
M5	2.6	1.232	10.0	44
B1	1.6	1.045	9.4	56
B2	2.9	0.827	9.5	41
B3	2.4	1.063	9.8	42
B4	1.3	0.520	9.2	76

It can be observed in the table that differences in rheological behaviour led to changes in the surface drying time of the glaze layer that formed (t_s). In fact, Fig. 3 shows that on raising the value of σ_0, surface drying time decreased, as was to be expected from the foregoing.

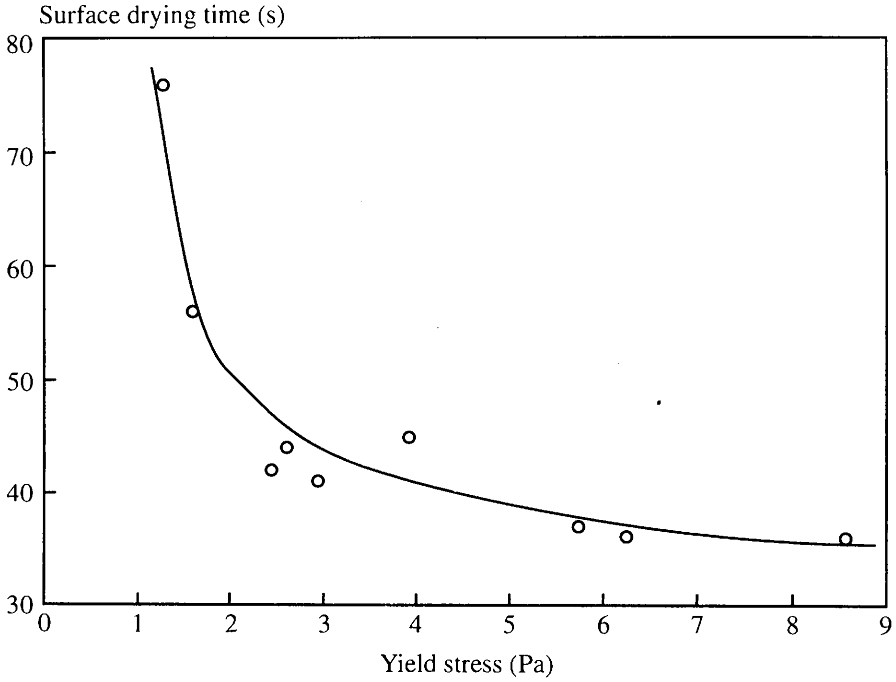


Figure 3. *Variation of surface drying time of the glaze layer versus yield stress of the suspension for the nine studied frits.*

The variations observed in the value of η_{100} indicate that at a shear rate of 100 s^{-1} the full breakup of the existing agglomerates had probably not yet been accomplished, and therefore the suspensions with higher values for σ_0, generally also exhibit higher values of η_{100}. Bearing this fact in mind, and taking into consideration that the variation interval of σ_0 is greater than that of η_{100}, it was decided to solely take parameter σ_0 into account for further study.

The causes for the variations that were observed in rheological behaviour might be due to a difference in surface charge of the particles caused by the differing pH of the medium, or could be caused by the surface adsorption of different types of ions stemming from frit dissolution. In both cases, the result would be reflected in a variation of the interparticle forces, and therefore in differences in the suspension's rheological behaviour, above all with regard to yield stress (σ_0).

It was attempted to relate the rheological behaviour of the suspensions with their pH, but no clear dependency was found. For this reason, it was thought that the ions supplied by frit dissolution might play an important role in the rheological behaviour of the suspensions, owing to their adsorption onto the particles. It was thus decided to set up an experimental method to determine frit solubility (Section 2.2.3) during glaze suspension preparation, in order to be able to relate the variations in rheological behaviour of the suspensions with the type and quantity of ions supplied by the frit.

Table 2 lists the data obtained on determining the solubility of the nine tested frits.

Table 2. Frit solubility and yield stress values (σ_0) of the glaze suspensions prepared from the studied frits.

Frit	Concentration ($x10^3$ moles/l)				Solubility ratio (Sodium/Potassium)	σ_0 (Pa)
	Sodium	Potassium	Calcium	Magnesium		
M1	1.79	4.46	0.36	0.05	0.40	3.9
M2	3.92	5.72	0.63	0.03	0.69	5.7
M3	1.58	7.31	1.27	0.12	0.22	8.6
M4	1.86	5.53	1.3	0.13	0.34	6.2
M5	6.19	5.54	1.36	0.07	1.12	2.6
B1	10.81	2.40	0.73	0.06	4.51	1.6
B2	9.76	7.41	0.91	0.15	1.32	2.9
B3	13.19	3.64	0.62	0.06	3.62	2.4
B4	22.01	0.74	1.43	0.36	29.88	1.3

It can be inferred on examining these data that the major concentrations of solubilized elements are in some cases sodium (generally frits referenced B), and in others potassium (generally frits referenced M), while the calcium concentration is always considerably lower than the corresponding element that solubilizes in the greatest proportion. The quantity of magnesium may be considered negligible in all the tested frits. For this reason, only the sodium and potassium ions were taken into account in subsequent considerations.

Table 2 also details the yield stress values obtained for the glaze suspensions prepared using the various frits. It can be observed that the suspensions prepared from the frits that solubilized the largest amount of sodium exhibit lower yield stress than the ones in which frits had been used which solubilized a greater proportion of potassium. Therefore, on computing the sodium/potassium solubility ratio (Table 2), it can be observed that raising this ratio reduces the value of σ_0, which is a potential type of decrease (Fig. 4). A similar relation is obtained for η_{100}, although this has a narrower variation interval.

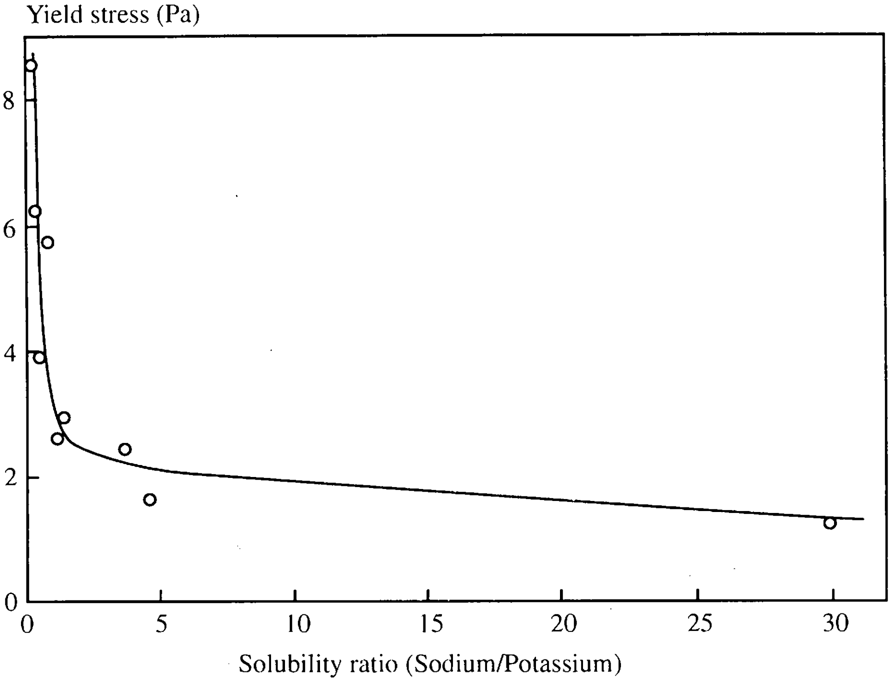


Figure 4. *Variation of yield stress in the suspensions prepared from the nine studied frits as a function of the sodium/potassium solubility ratio.*

These outcomes can be explained if we consider that the adsorption of sodium ions, whose hydrated radius is larger than that of the potassium ions [24][25], will give rise to an increase in the size of the electric double layer (specifically of δ), which will raise interparticle repulsion, and therefore yield a more dispersed suspension (deflocculated) than in the case of a preferential potassium ion adsorption.

Taking heed of the differences that could be observed between the suspensions that were prepared with the various tested frits, two were chosen (M3 and B1), having quite different characteristics, with a view to determining more clearly how various factors (pH, water hardness and additives) impacted the rheological behaviour of the glaze suspensions.

3.2 INFLUENCE OF GLAZE SUSPENSION pH ON THE SUSPENSION'S RHEOLOGICAL BEHAVIOUR

A suspension's pH must also affect its rheological behaviour, owing to the variations that it can cause in particle charge and the shift in the frit solubility equilibria, which can also lead to differences in surface charge and solubilized ion concentrations. It must also be borne in mind that a variation in the pH may entail differences in the surface adsorption equilibria of polyelectrolytes like TPF and CMC.

A glaze suspension may exhibit a different pH according to the frit used, and the nature and proportion of the additives the suspension contains. It could be observed in Table 1 that the pH interval of the tested suspensions ranged from 9.4 to 10.4. It was therefore decided to run a series of experiments with a view to determining how a variation in pH would affect the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1. The pH interval considered ranged from 8 to 11.2.

The results obtained have been plotted in Fig. 5. The figure shows that an increase in pH has a deflocculating effect on the suspension (σ_0 and η_{100} decrease). However, just as in the foregoing cases, the variation interval of σ_0 with pH is greater than the one found for η_{100}. It can furthermore be observed that the effect of the pH is more striking in the glaze suspension prepared with frit B1. In this suspension, at pH values exceeding 9.5, σ_0 rises slightly, likely due to the compressed double layer effects caused by the medium's ionic force (Fig. 2).

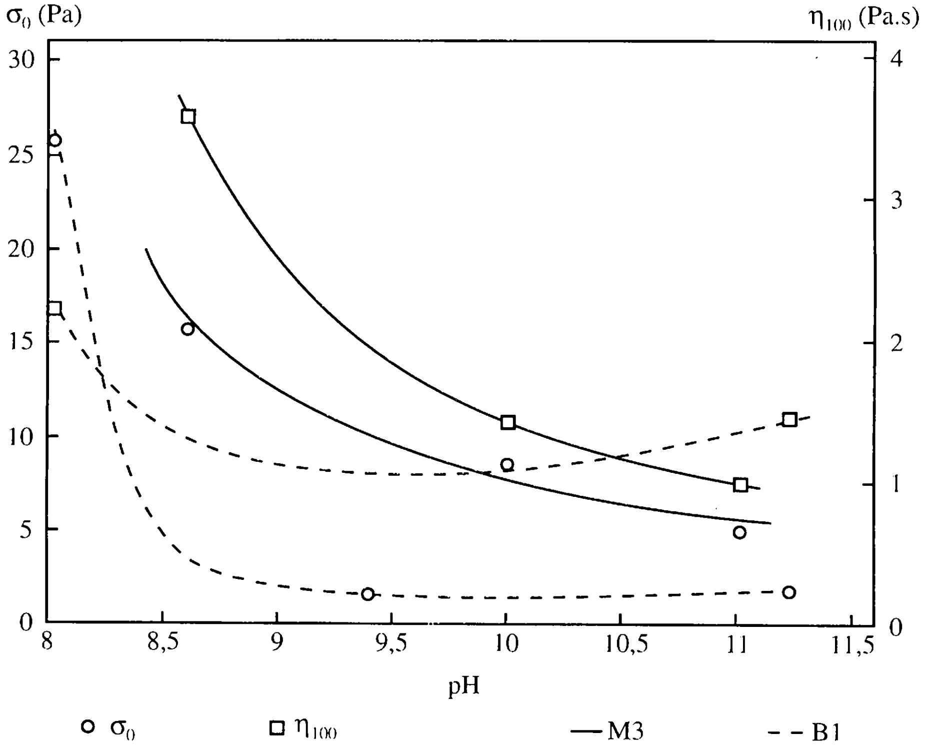


Figure 5. Variation of the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1 as a function of pH.

These results show that the variations in the rheological parameters (η_{100} and especially σ_0) are quite considerable as a result of pH changes in the suspension, although they also depend upon the characteristics of the frit used. Therefore, with the purpose of obtaining dispersions with stable rheological behaviour, not only should this variable (pH) be controlled, but the possible origins of its variation should also be analyzed.

3.3 INFLUENCE OF THE CALCIUM CONTAINED IN THE WATER USED FOR PREPARING THE GLAZE SUSPENSION, ON THE SUSPENSION'S RHEOLOGICAL BEHAVIOUR

One of the cations usually found in glaze suspensions is that of calcium from the water used for preparing or milling the suspension. The concentration of this ion usually lies in the range 100-250 ppm ($2.5 \cdot 10^{-3}$ and $6.25 \cdot 10^{-3}$ moles/l), depending on whether the water has been decalcified.

In an intent to determine how this cation influences the rheological behaviour of the suspensions, glaze suspensions were prepared from frits M3 and B1, to which the following calcium concentrations were added: 50, 100 and 300 ppm.

The results have been plotted in Fig. 6. The figure shows that yield stress (σ_0) rises in both cases, as does viscosity at high shear rates (η_{100}) on raising the amount of calcium that was added to the suspension.

Consequently, the calcium ion produces flocculation of the suspension, although as set out in the introduction, this effect should only be reflected in the values of σ_0 and not in those of η_{100}. The modification arising in the latter parameter suggests that the structure formed by the suspension owing to the presence of the calcium ion, is not fully broken up on raising the shear rate, i.e. there is no flow of individualized particles (if such had been the case, the value of η_{100} would be independent of the calcium ion concentration in the medium) [33][34]. However, it can be observed that the variation interval for the value of σ_0 is greater than the one corresponding to η_{100}.

The same figure also shows that the variation obtained in the value of σ_0 for suspension M3 is more marked than that observed for suspension B1. These findings indicate that the effect of the calcium ion contained in the suspension water will depend on the characteristics of the frit employed.

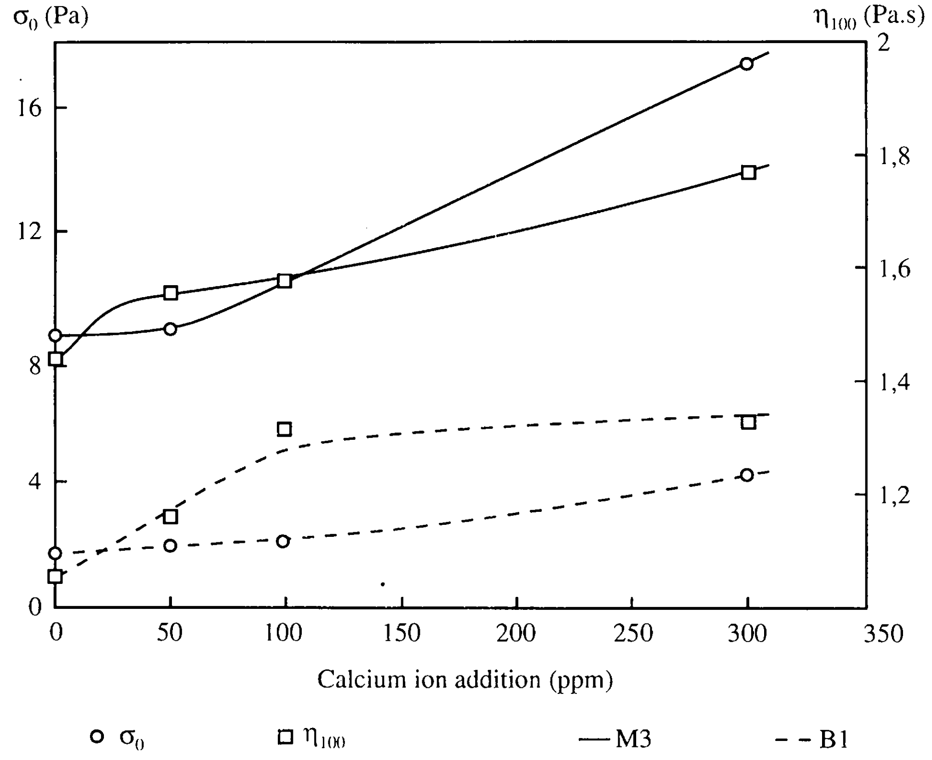


Figure 6. *Variation of rheological behaviour (σ_0 and η_{100}) as a function of the calcium ion addition to the suspensions prepared from frits M3 and B1.*

On the other hand, the rise in yield stress with the increase in the proportion of calcium ions present in the suspension, will give rise to a drop in the surface drying time of the glaze layer formed from this suspension. Such was the case of the suspension prepared from frit B1, in which, after adding 100 ppm of the calcium ion, surface drying time of the glaze layer that formed fell from 56 to 34 s.

The calcium ion can cause aggregation in the suspension as a result of its adsorption onto the particle surface, since on being a smaller cation than sodium or potassium, and having a larger charge, it produces a decrease in the extension of the double layer (lower δ). Furthermore, if a very high concentration of calcium is added, aggregation may also be due to the compressed double layer phenomenon.

3.4 INFLUENCE OF THE NATURE AND PROPORTION OF THE ADDITIVES USED IN PREPARING THE GLAZE SUSPENSION, ON THE SUSPENSION'S RHEOLOGICAL BEHAVIOUR

As has been observed, frit solubility and hardness of the water employed in preparing the glaze suspensions will make these suspensions exhibit differing rheological behaviour. However, the use of additives allows modifying such behaviour and make it better suited to the process and/or product to be fabricated.

This part of the study sets out the results of the determination of how the sodium carboxymethylcellulose binder, the sodium tripolyphosphate deflocculant and common salt, all of which are commonly used additives in these kinds of suspensions, affected the rheological behaviour of the glaze suspension.

3.4.1 Effect of the sodium carboxymethylcellulose binder (CMC)

A certain amount of CMC (around 0.3 wt% in respect of the dry solid) is added to virtually every glaze suspension, mainly to enhance the cohesion of the glaze layer and its bonding to the dry body. However, certain authors report [29-32] that this additive is adsorbed onto the particles and besides acting as a binder also serves as a deflocculant for the suspension.

To verify this effect, glaze suspensions were prepared from frits M3 and B1, to which varying proportions of CMC were added: 0, 0.1, 0.3 and 0.6 wt% (in respect of the solid). The results obtained after characterizing the rheological behaviour (σ_0 and η_{100}) of these suspensions have been plotted in Fig. 7.

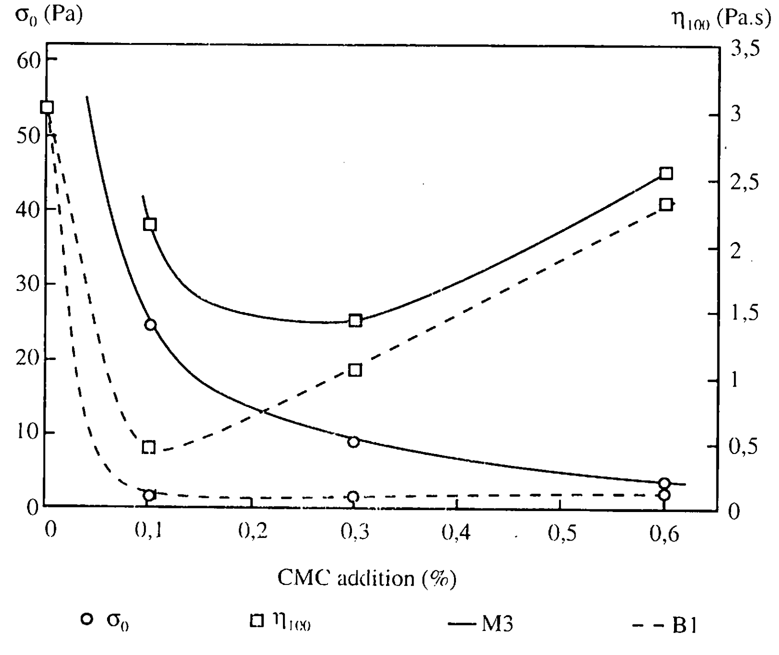


Figure 7. Variation of the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1 as a function of the CMC proportion.

The figure shows that the glaze suspensions without CMC are highly flocculated, since they exhibit high values for σ0 and η100 (in the case of suspension M3 these variables could not be determined owing to the difficulty involved in handling this suspension because of its high viscosity when left to stand). Adding CMC caused the suspension to deflocculate (sharp drop in σ0 and a less marked decrease in the value for η100), while being more effective in the glaze suspension prepared with the frit that exhibited the greatest sodium solubility (B1).

On the other hand, on observing the variation curve of η_{100} with the added CMC proportion, the two tested suspensions are shown to present a minimum, which is due to the concurrent action of two opposing phenomena (schematically depicted in Fig. 8).

Actually, the drop in the value of η_{100} on raising the CMC proportion, is progressively compensated by the rise in viscosity of the dispersing medium (water-CMC). This is why in the suspension prepared from frit B1 there is also a slight increase in the value of σ_0 on adding 0.6 wt% CMC instead of 0.3%. In this last case, the rise in σ_0 failed to produce a drop in the surface drying time of the glaze layer (t_s), rather the opposite occurred, since for the suspension with 0.3 wt% CMC, a value was obtained for t_s of 56 s, whereas at 0.6 wt% drying time was 89 s. This happened because the increase in viscosity of the liquid slowed down the suction process.

These results show that controlling the added proportion of CMC is of the greatest importance when it comes to obtaining suspensions with identical rheological behaviour, owing to CMC's twofold effect as deflocculant-thickener.

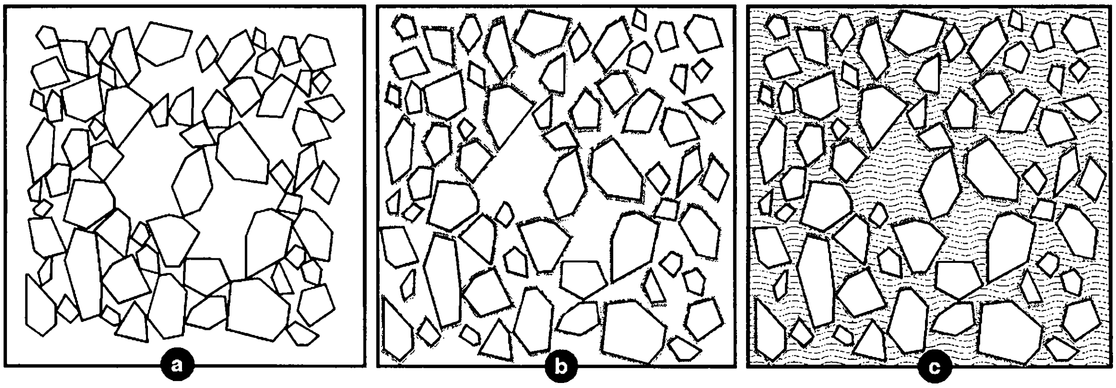


Figure 8. *Schematic illustration of the twofold effect of CMC on a glaze suspension:a) without CMC, b) small proportion of CMC (dispersant), c) high proportion of CMC (thickener).*

3.4.2 Effect of the sodium tripolyphosphate deflocculant

The deflocculant usually employed in preparing glaze suspensions is sodium tripolyphosphate (TPF), which is reported [26-28] to adsorb onto particles, capturing ions of a flocculant nature (divalent ions). The standard amount used is 0.1 wt% (in respect of the solid). This is why the proportions tested lay around this figure, namely: 0, 0.05, 0.1 and 0.2 wt%.

Fig. 9 depicts the data resulting from the determination of the rheological behaviour (σ_0 and η_{100}) of the glaze suspensions that were prepared from frits M3 and B1 with the above TPF proportions. The figure also shows that a deflocculant addition to a glaze suspension produces a drop in the yield stress and in the value of the viscosity at high shear rates. The former effect is more marked than the latter, which suggests that the effect of the deflocculant basically involves a reduction of the agglomerate content in the suspension.

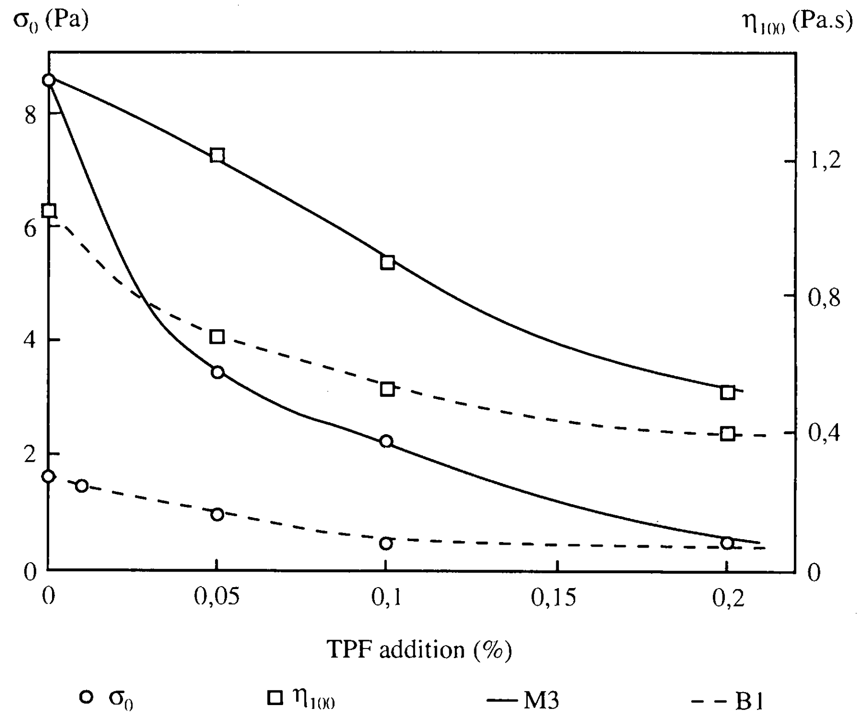


Figure 9. *Variation of the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1 as a function of the TPF proportion.*

These data allow inferring that adding deflocculant makes it possible to obtain suspensions prepared from frits with differing characteristics, which will however exhibit quite similar rheological behaviour (M3 with 0.2 wt% TPF and B1 with 0.1 wt% TPF).

In this case, the drop in yield stress of the suspension raised surface drying time of the glaze layer, as was to be expected (36 s for suspension M3 without deflocculant, and 57 s for the same suspension containing 0.1% TPF).

3.4.3 Effect of common salt

Although the reason for using common salt is at present not really fully clear, this electrolyte is often employed in the industry as an additive to glaze suspensions in proportions ranging from 0.05 to 0.1 wt% (in respect of the solid). The tested proportions were therefore: 0, 0.05, 0.1 and 0.15 wt%.

The results obtained have been reported in Fig. 10 of the characterization of the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1 with the above proportions of common salt. The figure shows that the salt additions have a flocculating effect on both suspensions (increase of σ_0 and η_{100}) across the whole interval of tested salt proportions.

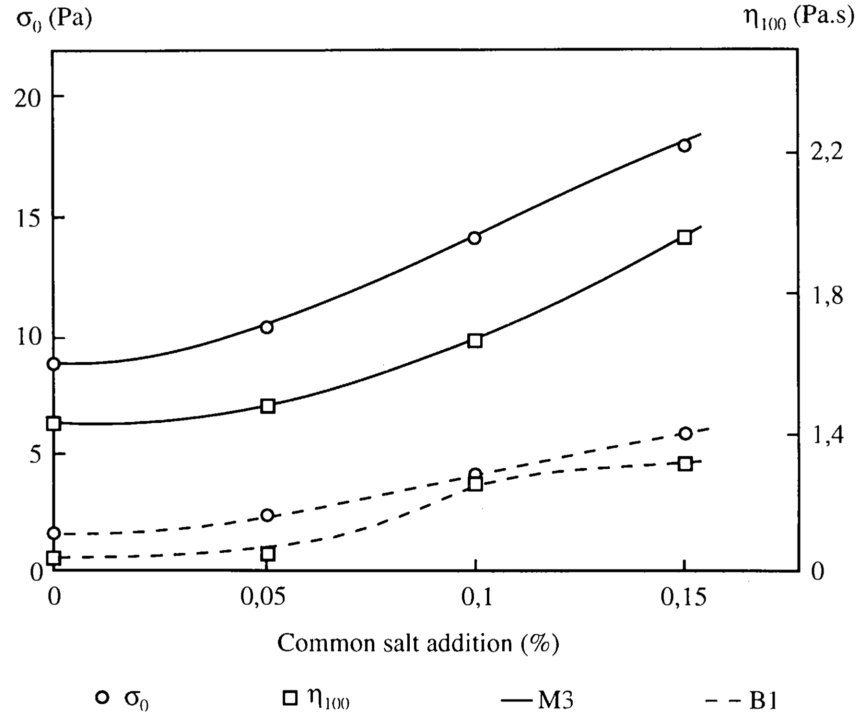


Figure 10. Variation of the rheological behaviour (σ_0 and η_{100}) of the suspensions prepared from frits M3 and B1 as a function of the common salt proportion.

The figure reveals that the σ_0 variation interval, just as in the foregoing cases is wider than the η_{100} variation interval. It can also be observed that the effect of common salt on σ_0 is more marked in the suspension prepared from frit M3, which solubilizes a smaller amount of sodium.

As was to be expected, the rise in the yield stress of the suspension on adding common salt, produces a drop in surface drying time of the glaze layer obtained from this glaze suspension. An 0.1 wt% common salt addition to the suspension prepared from frit B1 brings surface drying time back from 56 to 25 s.

The effect that common salt has on the rheological behaviour of these glaze suspensions might be caused by the fact that its use in relatively high proportions in the suspension produces the compressed double layer effect discussed above.

4 CONCLUSIONS

- It has been shown that the rheological behaviour, assessed on the basis of yield stress (σ0) and viscosity values at high shear rates (η100) of the glaze suspensions, is a function of the characteristics of the frit used in glaze suspension preparation.

- After setting up a test for the determination of frit solubility, an experimental relation was found between the suspension's yield stress and frit solubility (solubilized sodium/potassium ratio).

- It was furthermore shown that minor variations in the pH of a suspension produced noticeable differences in the suspension's rheological behaviour. Generally, on raising pH, the particles in the suspension broke up, (η100 and especially σ0 dropped). The magnitude of these variations was observed to also depend on the characteristics of the frit used.

- The variation in the rheological behaviour of the glaze suspensions was determined ($\sigma 0$ and $\eta 100$) as a result of the presence of calcium and certain additives (CMC, TPF and common salt). The magnitude of the variation was also shown to depend on the characteristics of the frit used.

- It may in summary be stated that the calcium and sodium ion (from common salt) give rise to particle agglomeration (flocculation of the suspension), via a mechanism involving compression of the electric double layer that surrounds the charged particles. However, both CMC and TPF cause particle aggregates to break up (deflocculation of the suspension) by an electro-steric mechanism, as both anionic polymers are adsorbed onto the charged particles. In the TPF, this deflocculating effect is also caused by TPF's tendency to capture divalent ions. In the case of CMC, a certain competition arises between the deflocculating effect and the raised viscosity of the suspending medium (water).

- Yield stress ($\sigma 0$) is one of the rheological parameters that underwent the greatest modification throughout the tests, because of its sensitivity and dependency upon the suspension's agglomeration state. A relationship was established between this parameter and surface drying time (ts) of the glaze layer that formed. Generally, raising $\sigma 0$ lowered the value of ts. This parameter may therefore be considered suitable for assessing how the suspension will behave during the glazing operation.

- The results obtained in the study allow concluding that in order to obtain a glaze suspension with appropriate rheological behaviour, minimizing the defects that arise as a result of an incorrectly implemented glazing operation, while obtaining good properties in the resulting final glaze coating, it will be necessary to use additives in proportions that will be a function, among other factors, of the characteristics of the frit employed and the pH of the suspension involved.

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