

QUALITY CONTROL OF TRIPOLYPHOSPHATES USED IN PRODUCING ENGOBES AND GLAZES

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1. ABSTRACT

To ensure product quality, control is required of the materials used in production. However, most ceramic tile manufacturers consider the quality control currently performed on the additives (binders and deflocculants) used in preparing engobes and glazes to be scarce and incomplete.

The present work proposes a plan to control the quality of the most widely used deflocculant in glaze and engobe production, sodium tripolyphosphate (STP). The plan establishes the tests to be conducted to characterise this deflocculant and thus avoid changes in the production process owing to variations in STP properties.

To establish the tests it has been necessary to characterise various sodium tripolyphosphates and study how the variation of certain STP properties affect the behaviour of the suspensions made up with this additive. The paper sets out the most relevant results.

2. INTRODUCTION

Various types of deflocculants can be used in preparing engobe and glaze suspensions. However, sodium tripolyphosphate is the most widely used deflocculant^[1] owing to its cost/efficiency ratio.

[1] MARCO, J.; GIMENO, R; ET. AL. *Rheological behaviour of glaze suspensions. Influence of frit solubility, pH, water hardness and additives.* Ceram. Acta, 8(6), 35-51, 1996.

No control tests are normally run on the additives used for adjusting suspension rheological conditions, owing to the small proportions involved. However, quality control of these additives is needed because of their considerable effect on the properties of these suspensions and the resulting coatings. Thus, tests are usually not performed on sodium tripolyphosphate (STP) to determine its characteristics, and hence decide whether or not to use it in the production process.

Appropriate STP control will enable suppressing the problems stemming from variations in the deflocculation state of the suspension caused by changes in STP characteristics. To establish which STP controls are required, it is necessary to determine how it works and how STP characteristics can affect the way it works.

As all polyphosphates, STP is a good deflocculant because it acts in two ways ^[2-6]:

- It is adsorbed onto the particles, producing interparticle repulsion by electrosteric stabilisation.
- It eliminates flocculant ions such as Ca (II) and Mg (II), by forming stable complexes with them.

In both cases, for the STP to be effective, it must be dissolved, as it is the $P_3O_{10}^{5-}$ anion that acts. Thus, variables that affect STP solubility can affect its deflocculating capability.

3. SODIUM TRIPOLYPHOSPHATE (STP) PRODUCTION AND CHARACTERISTICS

Sodium tripolyphosphate ($Na_5P_3O_{10}$) appears at ambient temperature in three crystalline forms. Two of these are anhydrous, termed form I (STP-I) and form II (STP-II), and the third is hexahydrated ($STP \cdot 6H_2O$). The structure of the anhydrous species differs in sodium cation coordination, which is completely octahedral in form II, and tetrahedral and octahedral in form I. Both forms can be identified by IR-spectroscopy, X-ray diffraction (XRD), as well as tests based on the different hydrating tendencies of these forms ^[7].

Commercial STPs are produced by drying a suspension or solution of phosphates (NaH_2PO_4 , Na_2HPO_4) or sodium pyrophosphates ($Na_2H_2P_2O_7$, $Na_2P_2O_7$) with the relevant stoichiometric proportions. Drying is the critical production stage, as the way it is done and the equipment used condition crystal size and distribution, factors that largely determine process output. The dry material is subsequently calcined, which will definitively determine the conversion to anhydrous sodium tripolyphosphate, as well as the relation between the two crystalline forms (I and II). Finally, the material is conditioned and graded in sizes by different techniques ^[7].

Other operating variables being equal, STP dissolution in water is conditioned by two opposing factors, closely related to the crystalline forms it comprises ^[7]:

[7] KIRK-OTHMER. *Encyclopedia of Chemical Technology*. 3rd ed. New York: John Wiley, 1982. Vol 17, Phosphoric acids and phosphates, p. 426-472.

- The different solubility of the crystalline phases. Form I is more soluble than form II, and the latter is more soluble than the hexahydrated form.
- The crystallisation of the hydrated species and therefore, the elimination of part of the dissolved STP. Though form I exhibits a greater dissolution rate, it tends to produce the rapid crystallisation of the hexahydrated species. However, form II oversaturates easily, i.e., keeps higher dissolved STP concentrations than equilibrium concentrations without precipitating the hydrated form.

Besides crystalline-phase type and proportion, further factors such as stirring, addition order, etc., are also of great importance in the dissolution and possible crystallisation of the hydrated form.

The presence of impurities in sodium tripolyphosphate can also affect its deflocculating efficiency to a greater or lesser extent. The most common STP impurities, sometimes found in proportions of up to 1%, which are generated in the production process, are pyrophosphates ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, $\text{Na}_2\text{P}_2\text{O}_7$) and trimetaphosphates ($\text{Na}_3\text{P}_3\text{O}_9$). There may also be smaller quantities of unreacted phosphates such as long-chain polyphosphates ($\text{Na}_3\text{P}_3\text{O}_9(\text{NaPO}_3)_n$). The STPs may also be accompanied by chlorides and sulphates, associated with the water added in product preparation.

4. OBJECTIVE

The purpose of the present study was to establish the controls required for the STPs used as deflocculants in ceramic engobe and glaze suspensions, to assure STP incorporation into the manufacturing process will not modify working conditions.

5. MATERIALS

The STPs used in this study were supplied by different companies that market and consume this product. Six STPs used in preparing engobe and glaze suspensions were employed, referenced: STP-1, STP-2, STP-3, STP-4, STP-5 and STP-6.

A suspension prepared with a standard white kaolin used for preparing engobes, with a specific surface of $17.4 \text{ m}^2/\text{g}$, was used to determine the deflocculating power of the different STPs.

6. EXPERIMENTAL PROCEDURE

6.1.- CHARACTERISATION OF INDUSTRIAL STPS

Six industrial STPs were characterised by determining their chemical analysis to establish the $\text{P}_2\text{O}_5/\text{Na}_2\text{O}$ ratio, possible presence of impurities, type of crystalline structure they comprised, and their particle or granule-size distribution, as this could affect the STP dissolution rate.

6.1.1.- Chemical analysis

The STP chemical composition was determined by X-ray fluorescence spectrometry by wavelength dispersion using reference standards assuring measurement traceability.

6.1.2.- Identification of crystalline structures

The crystalline structures of the different STPs were identified by XRD of the powder sample. The crystalline phases present were identified using the JCPDS files for pure crystalline phases.

6.1.3.- Particle/granule-size distribution

Laser diffraction was used to determine the particle / granule-size distribution of the tested STPs. The dry module was used in which the material is fed into the apparatus with an air injection and vacuum system, or by free fall if granulated material is involved. The end particle/granule-size distribution is found according to the Fraunhofer diffraction theory.

6.2.- DETERMINATION OF THE DEFLOCCULATION CAPABILITY

The deflocculation curve of the clay suspension prepared with a 55 wt% solids content was determined to test STP deflocculation capability.

The determination was run in batches, preparing a clay suspension for each deflocculant percentage to be tested. The suspensions were prepared in a fast laboratory alumina ball mill, milling for 10 minutes.

The deflocculant was generally added as a solid to the mill charge. On certain occasions, specified in the study, the addition took place as a solution, with a 2% deflocculant concentration.

After milling, suspension viscosity was determined on a torsion wire viscometer, estimating thixotropy by measuring the rise in suspension viscosity after a 6-min stand.

7. RESULTS

7.1.- CHARACTERISATION OF INDUSTRIAL STPS

Table 1 presents the chemical analysis of the six deflocculants together with moisture content and P_2O_5/Na_2O mass ratio calculated from the chemical analysis.

		STP-1	STP-2	STP-3	STP-4	STP-5	STP-6
Composition (wt%)	P ₂ O ₅	57.6	56.0	56.7	57.4	52.9	63.1
	Na ₂ O	42.0	41.9	41.2	40.4	40.9	35.9
	SiO ₂	<0.03	0.16	0.11	0.20	0.16	<0.03
	Cl ⁻	0.08	0.18	0.16	<0.03	1.4	<0.03
	SO ₃	0.23	1.3	1.5	<0.10	5.6	<0.1
Moisture content (%)		0.05	0.79	0.46	0.20	0.06	2.99
P₂O₅/Na₂O		1.37	1.34	1.38	1.42	1.29	1.76

Table 1. Test deflocculant composition, moisture content and P₂O₅/Na₂O mass ratio.

If it is taken into account that the P₂O₅/Na₂O mass ratio of pure sodium polyphosphate is 1.37 (57.9% P₂O₅ and 42.1% Na₂O), product STP-6 can be observed to exhibit a much higher P₂O₅ content than the theoretical value. Its effectiveness as a deflocculant can therefore be expected to be different^{[8][9]}, as it is either made up of longer-chain sodium polyphosphates (with a larger P₂O₅/Na₂O mass ratio), or it could contain other phosphates with a greater P₂O₅/Na₂O mass ratio besides STP.

Deflocculant STP-5 contains an important percentage of chlorides and sulphates, which, as mentioned above, are anions that have been incorporated in the production process. As flocculating ions are involved^[10], it can be assumed that this deflocculant is not as effective as others with similar characteristics, which do not bear these impurities.

Table 2 sets out the XRD data for the crystalline structure identification, expressed as the intensity of the representative peak for each identified phase by counts per second (cps).

Deflocculant	Intensity (cps)			
	STP-I	STP-II	STP-6H₂O	NaPO₃
STP-1	1197	2820	--	--
STP-2	--	2490	86	--
STP-3	2228	1225	112	--
STP-4	--	2775	--	--
STP-5	2480	2683	--	--
STP-6	--	1176	1163	1384

Table 2. Crystalline structures present in the test deflocculants.

[8] MANFREDINI, T.; PELLACANI, G.; ET AL. Monomeric and oligomeric phosphates as deflocculants of concentrated aqueous clay suspensions. *Appl. Clay Sci.*, 5, 193-201, 1990.

[9] MANFREDINI, T.; PELLACANI, G.; ET AL. Some general considerations on the rheological behaviour of aqueous clay suspensions: dependence on the physico-chemical properties of inorganic salts, calcium (II) ion presence and grinding times. *Industrial Ceramics*, 9(2), 58-62, 1989.

[10] BARBA, A.; ET AL. *Materias primas para la fabricación de soportes de baldosas cerámicas*. Castellón: Instituto de Tecnología Cerámica-AICE, 1999.

Besides forms II and hexahydrated STP (STP·6H₂O), deflocculant STP-6 contains sodium phosphate (NaPO₃). This indicates that its larger P₂O₅/Na₂O mass ratio (Table 1) is not caused by a longer-chain polyphosphate, but that it contains sodium phosphate, probably from an unsuitable production process.

It can also be observed that the samples in which the hexahydrated form was not detected (STP·6H₂O), were the ones whose moisture contents (Table 1) were lowest, suggesting that these parameters could be related.

Finally, form I and II content must be proportional to their peak intensities, as these two phases belong to the same crystalline system and the samples' coefficient of mass absorption is quite similar (the chemical compositions are similar). Thus, in deflocculant STP-5 forms I and II are found in similar proportions, products STP-2 and STP-4 are practically made up of form II, and in STP-3 and STP-1, the proportions of form I and II are inverted (STP-3 is richer in form I and STP-1 is richer in form II).

The data from the determination of the particle or granule-size distribution have been summarised in Table 3. The table presents the mean diameter (d_{50}), corresponding to the size below which 50% by volume of the particles are found for each tested sample. The high d_{50} values found for samples STP-5 and STP-4 indicate that they are granulated products.

Deflocculant	d_{50} (μm)
STP-1	27
STP-2	20
STP-3	51
STP-4	271
STP-5	345
STP-6	30

Table 3. Test deflocculant mean particle/granule size.

The differences in crystalline-phase content and particle sizes can basically be expected to affect the dissolution rate in water, while the differences in chemical composition will presumably affect deflocculating capability ^[11].

7.2.- DEFLOCCULATING CAPABILITY

Table 4 and Figure 1 set out the results of the determination of the deflocculation curve performed with each test STP. To simplify the data presentation, only the viscosity values found after a one-minute stand are shown, without indicating the corresponding data after a 6-min stand (thixotropy). Each STP can be observed to behave differently, in some cases with important differences.

[11] ANDREOLA, F.; POZZI, P.; ET AL. *Rheological behavior of an STP deflocculated kaolin*. Am. Ceram. Soc. Bull., 77(12), 68-71, 1998.

Deflocculant (%)	STP-1	STP-2	STP-3	STP-4	STP-5	STP-6
0.2	1030	1840	1400	2700	3850	--
0.3	--	1000	900	--	--	7000
0.4	875	1030	1320	1280	1720	4400
0.6	1180	1100	1980	1600	1780	6000
0.8	2000	1200	--	--	2275	--

Table 4. Results of the determination of the deflocculation curve with the six test deflocculants.

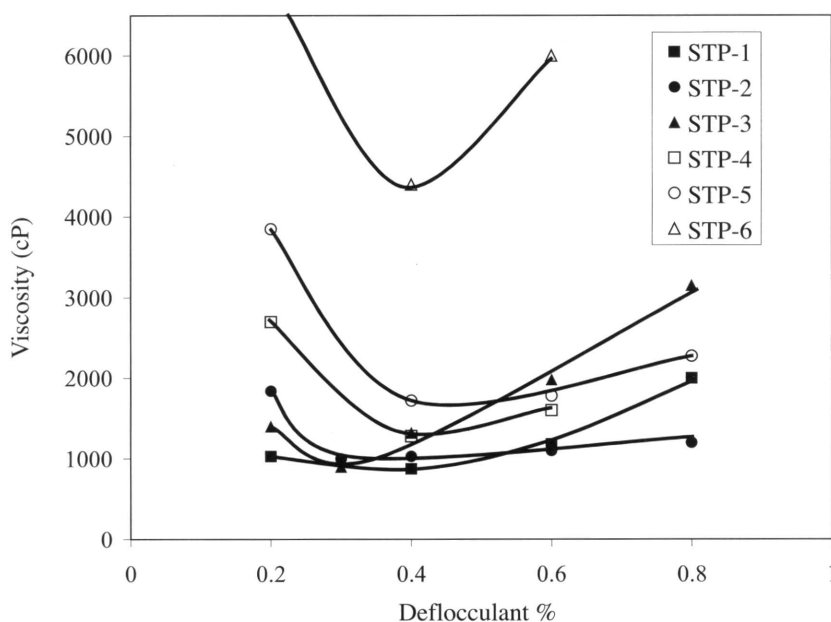


Figure 1. Deflocculation curves of the six test STPs.

Sample STP-6 was the least effective, as the curve minimum lay at higher viscosity values than for the other deflocculants.

The curve minimum practically coincided for deflocculants STP-1, STP-2 and STP-3, so that they can be considered equally effective. However, the curves were not wholly equivalent. STP-3 produced more pronounced overdeflocculation (greater rise in viscosity with deflocculant percentage) than STP-1, while that of the latter was greater than that of STP-2.

Deflocculants STP-5 and STP-4 exhibited an intermediate efficiency, which was considerably higher than that of STP-6. Although the minimum found for these deflocculants was at virtually the same deflocculant percentage, the viscosity at this minimum was considerably higher when deflocculant STP-6 was used.

7.2.1.- Effect of STP crystalline forms.

To attempt to determine the effect of forms I (STP-I) and II (STP-II) on STP deflocculating capability, samples STP-2 (form II), STP-1 (largest proportion of form II) and STP-3 (largest proportion of form I) were chosen, which were not granulated and exhibited no important quantities of impurities.

The deflocculation curves found for these three deflocculants have been plotted again as solid lines in Figure 2. The curve minima practically coincide, and the arising overdeflocculation increased as form I content rose in the STP. These findings could be explained by taking into account the differences in solubility of the various crystalline forms: when form I dissolves, which is the most soluble, the hexahydrated form crystallises, which is the least soluble of the three forms. Hence, the larger the form I content, the longer it will take for the STP to dissolve, and therefore the least effective it will be.

To confirm whether the differences found were produced by the different solubility of each crystalline form, solutions were prepared at a 2 wt% concentration of the three selected STPs, and these were used to obtain the deflocculation curves. This STP concentration was chosen because it produced a transparent solution, which would not be the case at higher concentrations. The corresponding deflocculation curves have been plotted in Figure 2 as dashed lines.

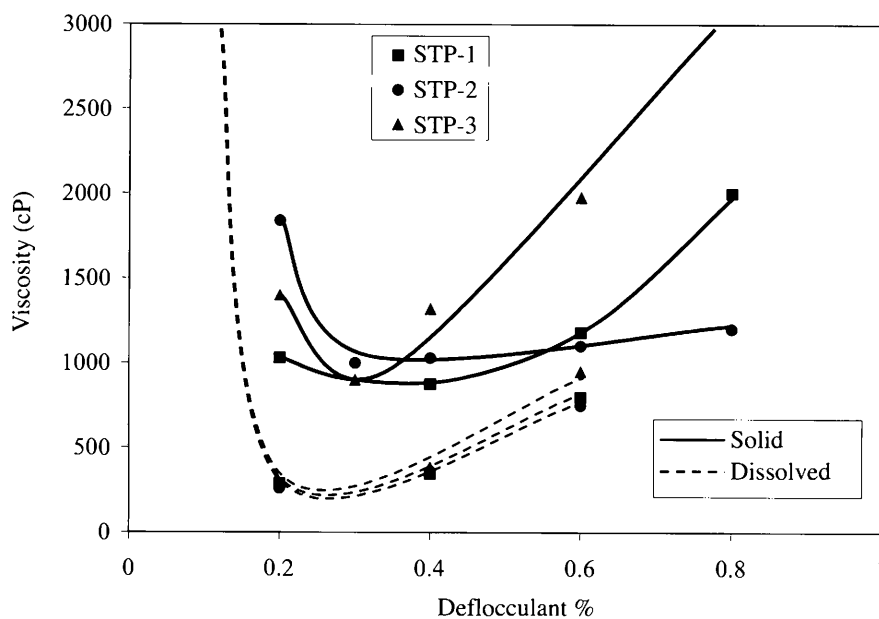


Figure 2. Influence of the presence of crystalline forms STP-I and STP-II on the deflocculation capability of sodium tripolyphosphate.

The curves obtained using the dissolved deflocculants were practically identical, which means that if the STP dissolves completely, there are no differences between the deflocculation capability of forms I and II. The minimum in the three curves also exhibited quite a lower viscosity than the viscosities found on adding the deflocculant in a solid form to the mill batch, indicating that the STP did not fully dissolve during clay suspension preparation.

To verify this, clay suspensions were prepared with deflocculants STP-2 and STP-3 in a proportion of 0.8%, as the overdeflocculation zone best allows observing the differences on using deflocculants with different proportions of form I and II. The suspensions were prepared using different dispersion times in a laboratory ball mill.

Figure 3 plots the viscosity of the clay suspensions prepared at an 0.8% concentration of deflocculants STP-2 and STP-3 versus dispersion time. When sample STP-2 was used, suspension viscosity hardly changed with stirring time, whereas the suspension viscosity found with STP-3 exhibited a considerable drop in viscosity with dispersion time, while both suspensions tended towards the same viscosity on raising dispersion time. This is because increasing dispersion time produces a better dissolution of form I (STP-3), yielding viscosities resembling those produced using sodium tripolyphosphate with form II (STP-2).

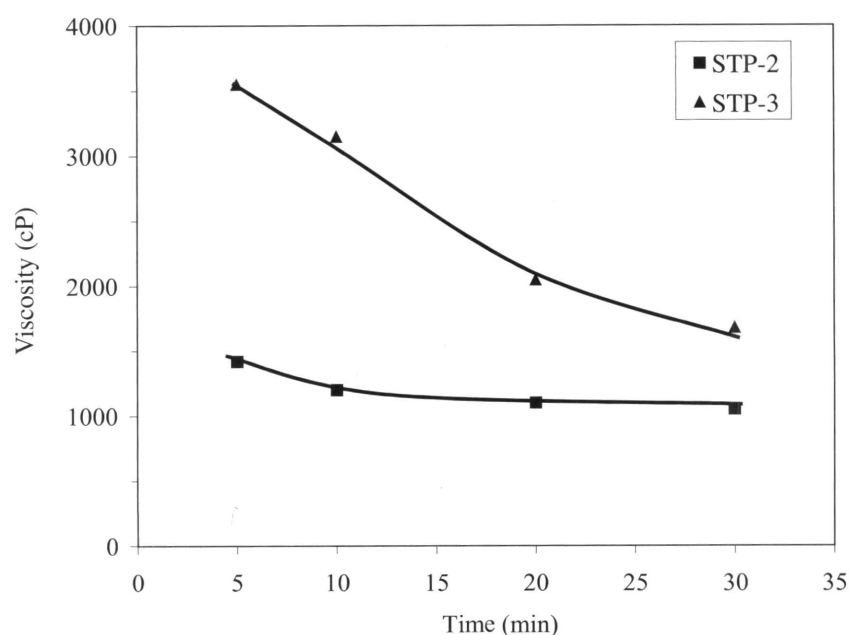


Figure 3. Variation of viscosity with milling time (STP-2 and STP-3).

The presence of STP crystalline forms I and II therefore only affect their dissolution rate. Differences are thus only found in their deflocculating capability in processes in which total dissolution is not attained, as can occur in preparing an engobe or glaze suspension.

To determine the effect of the hexahydrated form, the samples that only comprised STP and contained the hexahydrated form (STP-2 and STP-3) were oven dried at 110°C. XRD was then run to determine the crystalline species present, and drying was noticed to eliminate the hexahydrated form (Table 5). The deflocculating capability of these dry samples was then determined. No appreciable change was found.

Sample STP-2 was subjected to a hydration process, with the same purpose as in the foregoing case. This entailed dissolution and subsequent drying in mild conditions (35°C for five days). An XRD scan was run to verify whether the hydrated phase had been produced. The data are given in Table 5. The deflocculation capability of the hydrated sample was then determined, yielding the curve plotted in Figure 4, where it is compared with the non-hydrated sample deflocculation curve.,

Deflocculant	Intensity (cps)		
	STP-I	STP-II	STP-6H ₂ O
Dry STP-2	--	2938	--
Dry STP-3	2250	1240	--
Hydrated STP-2	--	--	3956

Table 5. Crystalline structures of the samples obtained after drying (dry STP-2 and dry STP-3) or hydration (hydrated STP-2).

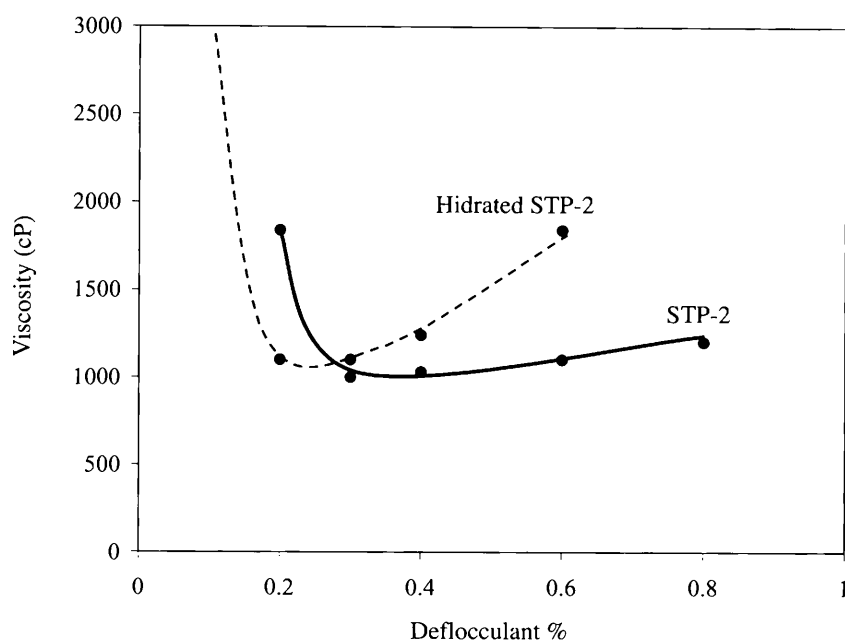


Figure 4. Influence of the presence of the form STP-6H₂O on STP deflocculating capability.

The hydrated sample was found to yield more pronounced overflocculation than the non-hydrated sample, even though the minimum lay at a lower deflocculant percentage. The behaviour was similar to that observed with the samples containing considerable quantities of STP-I, and could be due to the same effect, namely the different rate of dissolution of the hexahydrated form compared to the STP-II form.

7.2.2.- Effect of other compounds accompanying STP.

This section analyses the effect of the presence of NaPO_3 and sulphates sometimes found with STP on STP deflocculating capability.

The deflocculation curves (Figure 1) and XRD data (Table 2) show that the least effective test deflocculant (STP-6) contained NaPO_3 . Considering the low deflocculating capability of monomer phosphates ^{[8][9]}, lower efficiency of STP-6 was likely to be due to the presence of NaPO_3 .

NaPO_3 is not usually employed as a raw material for producing STP, so that this phase presumably arose during calcining. To verify this, STP-2 was calcined for 2 hours at 450°C . An XRD scan was run on the calcined sample. The data are reported in Table 6 (calcined STP-2), which also includes the non-calcined STP (STP-2) for comparative purposes.

Deflocculant	Intensity (cps)			
	STP-I	STP-II	STP-6H ₂ O	NaPO ₃
STP-2	--	2490	86	--
Calcined STP-2	--	1376	--	1129

Table 6. Crystalline structures present in calcined and non-calcined STP-2.

Figure 5 plots the deflocculation curves found with STP-2 and calcined STP-2. The findings confirm the negative effect of NaPO_3 on STP deflocculating capability.

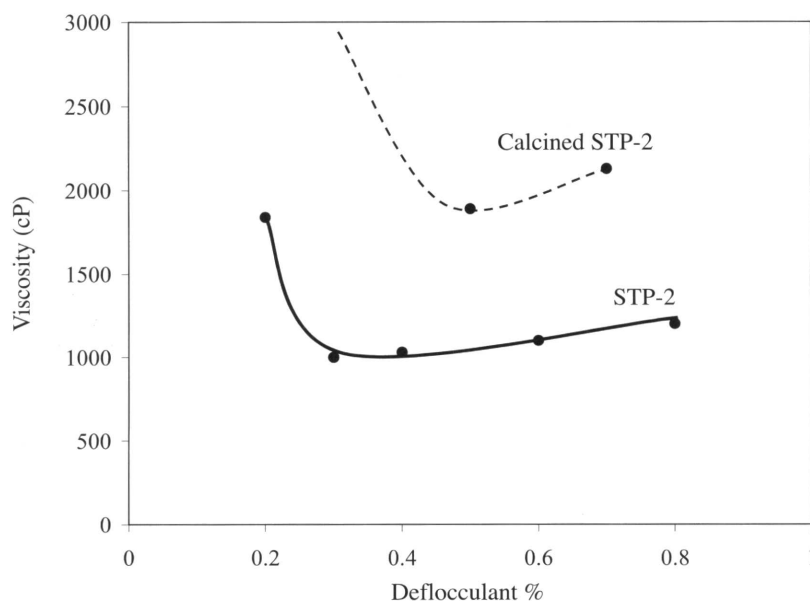


Figure 5. Influence of the presence of NaPO_3 on STP deflocculating capability.

[8] MANFREDINI, T.; PELLACANI, G.; et al. Monomeric and oligomeric phosphates as defloculants of concentrated aqueous clay suspensions. *Appl. Clay. Sci.*, 5, 193-201, 1990.

[9] MANFREDINI, T.; PELLACANI, G.; et al. Some general considerations on the rheological behaviour of aqueous clay suspensions: dependence on the physico-chemical properties of inorganic salts, calcium (II) ion presence and grinding times. *Industrial Ceramics*, 9(2), 58-62, 1989.

With regard to the presence of impurities, Figure 1 shows that STP-5 has an intermediate effectiveness between STP-6 and the rest. This could be due to two effects: it is granulated and contains sulphates. Gravimetry confirmed that soluble sulphates were involved, which act as flocculating substances in clay suspensions ^[10].

In order to eliminate the effect of granule size, a solution was prepared at a 2 wt% concentration, to determine the clay suspension deflocculation curve. The outcomes are presented in Figure 6, which also includes the experimental data for sample STP-1. This sample had a similar composition to STP-5, however without any sulphates. The figure shows that on starting with dissolved samples, STP-5 was less effective than STP-1, confirming the flocculating effect of the SO_4^{2-} impurities.

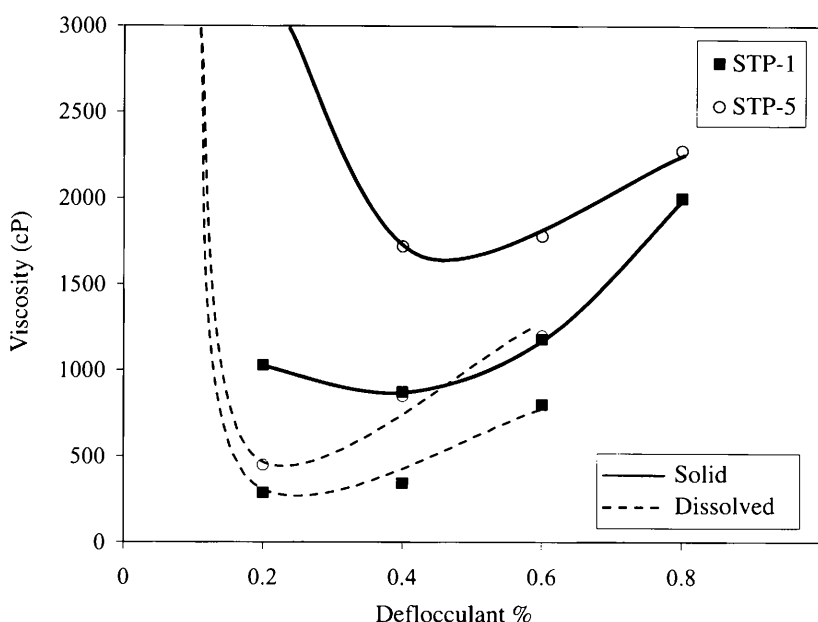


Figure 6. Influence of the presence of sulphates on STP deflocculating capability.

7.2.3.- Effect of particle/agglomerate size

To determine the influence of STP particle or agglomerate size, two samples were chosen with practically the same crystalline structures (mainly STP-II), one of which was granulated (STP-4) while the other was not (STP-2). To eliminate the effect of particle size, both samples were dissolved in water at a 2 wt% concentration, subsequently determining the respective clay suspension deflocculation curves. Figure 7 plots the findings. It shows that similar deflocculation curves were found on using solutions. The granulated samples therefore produced a delay in sample solubilisation, and hence lower deflocculant effectiveness when the deflocculant was added as a solid.

[10] BARBA, A.; et al. *Materias primas para la fabricación de soportes de baldosas cerámicas*. Castellón: Instituto de Tecnología Cerámica-AICE, 1999.

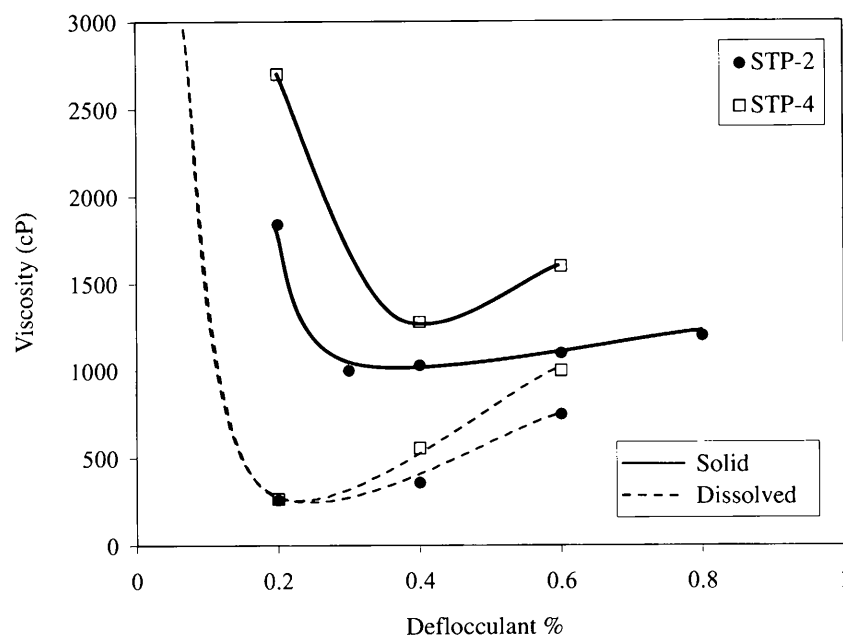


Figure 7. Influence of particle or agglomerate size on STP deflocculating capability.

8. CONCLUSIONS

The deflocculating capability was determined of sodium tripolyphosphates (STPs) used in industry to prepare engobe and glaze suspensions. Important differences were found amongst these products.

The differences were due to different causes:

- The presence of different crystalline forms (STP-I, STP-II and STP-6H₂O) in which STP can appear. These forms exhibit different dissolution rates, so that they could yield different results depending on operating conditions.
- When STP is accompanied by sodium phosphate (NaPO₃), its effectiveness is lowered owing to this compound's lower deflocculating capability.
- The presence of sulphates as STP impurities also reduces STP deflocculating efficiency owing to the flocculating character of this anion.
- The deflocculating capability of an STP can vary, depending on operating conditions, according to granule size.

In view of the findings, it may be inferred that complete STP control would require:

- Determination of its *chemical composition*, indicating whether the P₂O₅/Na₂O ratio is appropriate, and whether it contains sulphates or chlorides.
- Performance of *XRD analysis* to determine the STP crystalline forms and the presence of other crystalline forms such as sodium phosphate.

- Determination of its *particle or granule-size distribution*, especially for the granulated products.

These tests can be costly in time and money, especially for companies that do not possess suitable test instruments. Determining moisture content is a simple test and indicates the presence of the hexahydrated form ($\text{STP} \cdot 6\text{H}_2\text{O}$). If the product is granulated, its granule-size distribution can be controlled by dry sieving. However, obtaining the deflocculation curve is recommended as a control method, as it was found that variations in the deflocculation curve indicated whether sodium tripolyphosphate properties had altered.

ACKNOWLEDGEMENTS:

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9. REFERENCES

- [3] LAGALY, G. *Principles of flow of kaolin and bentonite dispersions*. «Appl. Clay. Sci.», 4, 105-123, 1989.
- [4] FAISON, J.; HABER, R.A. *Use of polyphosphates as deflocculants of alumina*. «Ceram. Eng. Sci. Proc.», 12(1-2), 106-115, 1991.
- [5] ANDREOLA, N. M. F.; ARGENTINA, L.B.; et al. *Addition of exhausted lime in ceramic bodies: possibilities for an environmentally compatible tile production. I: Rheological behaviour of slips*. «Tile & Brick. Int.», 8(1), 9-13, 1992.