TECHNIQUES FOR CONTROL OF SODIUM TRIPOLYPHOSPHATE IN CERAMIC SUSPENSIONS

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ABSTRACT

The ceramic production processes require raw materials of good quality to ensure that these materials function appropriately. Ceramists have difficulties in demanding quality of the raw materials for lack of more detailed knowledge of the raw materials role in the properties of the final product. Dispersing agents are important raw materials, which are not very well known, added to the ceramic suspensions to minimize the effect of particles gathering. Nowadays, sodium tripolyphosphate is the most widely utilized deflocculant due to its good performance; however, it presents fluctuations in its deflocculant capacity. In this work sodium tripolyphosphates produced by different manufacturers were compared. The behaviour of these materials was analysed by hydration and by the addition of other additives. This dispersing agent was characterized by X-ray fluorescence spectroscopy, with a view to establishing the presence of impurities and determining the content of P_2O_5 *and* Na_2O*. The amount of organic matter was taken in consideration. The identification of crystalline structures was carried out by X-ray diffraction, which is fundamental, because there are in nature different types of sodium tripolyphosphate structures with different rheological behaviour. With regard to the results, it was certified that its effectiveness increases with hydration and does not depend on the initial crystalline structure or on the sodium tripolyphosphate type, and the presence of the flocculation ion does not influence the deflocculation curves.*

KEY WORDS: sodium tripolyphosphate, ceramic suspensions, suspension stability

INTRODUCTION

The growing competition among industries, especially in the ceramic sector, is a factor that leads to scientific and technological development with a view to addressing the most intimate loss points, wastes and efficiency in the production process, so that quality can be improved, product prices can be reduced and greater profitability can be achieved. Quality control, mainly of the rheological properties, specifically viscosity, is fundamental to assure the characteristics and reproducibility of the process step – mainly of glaze and engobe slips, as well as final product performance. However, predicting solution viscosity is more important than controlling it, as well as looking for alternatives that improve process efficiency without increasing costs.

The deflocculants act on the particles surface inhibiting gathering through attraction forces. These forces can be fragile so that just gathering or sediments can be formed: or so strong, so that gatherings can be formed dispersible only with physical milling processes.[1] To solve these problems, ceramists use several types of organic additives, including, deflocculants or dispersants.

Any substance whose addition to a clay and water mixture makes the mass more fluid is called a deflocculating agent, or simply, a deflocculant. They can be hydroxides of monovalent cations, such as Na^+, K^+, NH_4^+, or salts of these cations that undergo hydrolysis in an alkali (Na_2CO_3 or Na_2SiO_3), or can be organic colloids such as tannic acid, humic acid or alkaline salts of these materials. In general, the addition of a deflocculant changes the clay to clay-Na^+, consequently increasing the repulsion among the particles and decreasing suspension viscosity.[2]

The deflocculant most widely utilized nowadays to prepare engobes and glazes is sodium tripolyphosphate (STP) due to its low cost/benefit ratio; however there are in nature different types of sodium tripolyphosphate, which have different crystalline structure and because of this they present different rheological behaviour. Sodium tripolyphosphate adsorbs onto the particles causing their repulsion due to the eletrosteric stabilization mechanism.

In this work sodium tripolyphosphate produced by different manufacturers were compared. The behaviour of these materials was analysed by hydration and by the addition of other additives.

SODIUM TRIPOLYPHOSPHATE (STP) STRUCTURE AND PROPERTIES

Sodium tripolyphosphate or pentasodium triphosphate, $Na_5P_3O_{10}$ is a pentasodium salt of a tripolyphosphate anion. Three distinct crystalline structures are known: two are anhydrous and a third one is hexahydrated. Sodium tripolyphosphate is a highly efficient deflocculant and constitutes a particular case because it produces very fluid slips with a high solids content. The action mechanism uses the fact that the phosphate anion is one of those preferably adsorbed on the clay particle, raising the negative charge and consequently raising the Zeta potential, which contributes in a determinant mode to a higher dispersant effect.

Sodium tripolyphosphate (STP), as all the polyphosphates, is a good deflocculating agent by acting in the following way: it adsorbs over the particles causing their repulsion due to the eletrosteric stabilization mechanism or elimination of the flocculating ions, such as Ca(II) or Mg(II), through the formation of stable complexes with these. In both cases, it is necessary for the STP to dissolve to make it effective, since it is the anion $P_3O_{10}^{5-}$ that is acting. Thus, the variables that can change the solubility of the STP will affect its deflocculating capacity.[3,4]

Pentasodium triphosphate, $Na_5P_3O_{10,}$ is found in nature in three crystalline structures, two of them anhydrous and a third one hexahydrated. The anhydrous structures are considered stable at room temperature and exist with each other in nature, differing by the ionic coordination of their cations.

The anhydrous structure II presents octahedral coordination of its oxygen while anhydrous structure I presents a tetrahedral shape. This means that the arrangement of its sodium atoms is surrounded by four oxygen atoms. In both anhydrous structures the electrostatic bond cation-anion forms a continuous three-dimensional net, but in the structure II the arrangement is flat, like a leaf.

The hexahydrated structure can be formed by the addition of any anhydrous structure to water or by the hydrolysis of sodium trimetaphosphate in an alkali solution. A quick hydrolytic degradation of the pyrophosphate and phosphates occurs at approximately 1000° C. The salts of sodium tripolyphosphate are produced by thermal dehydration by an intimate mixture of phosphate salts containing a correct metal/phosphorus ratio. Although a great number of STPs are known, only the pentasodium ones are important. That is why a variety of commercially products made come from phosphoric acid burning.[3].

The crystalline structure of the STP has different properties such as solubility, dissolution, etc.; for example, it is known that anhydrous structure I is more soluble than the anhydrous structure II, which is more soluble than the hexahydrated form.[5]

The hexahydrated structure can be converted to anhydrous structures if subjected to thermal treatment, without degrading the sodium tripolyphosphate and without changing its properties. When subjected to 350° C it forms the anhydrous structure II and when subjected to 550° C it forms the anhydrous structure I.[6].

OBJECTIVE

Sodium tripolyphosphates are used in the stabilization of ceramic suspensions. In this work, deflocculants produced by different manufacturers were compared, considering the effect of sodium tripolyphosphate hydration before being added to the suspensions. In order to perform the tests, it was necessary to characterize different sodium tripolyphosphates and to study how the variation of some of their properties affects the behaviour of suspensions prepared with those additives.

The crystalline structure of the sodium tripolyphosphate was analyzed by X-ray diffraction, and it is a fundamental factor due to the existence of different structures in nature, which strongly affect the rheological behaviour of suspensions. Hydration studies of the sodium tripolyphosphate allowed analyzing the formation of crystalline phases. Commercially the most common process to obtain the sodium tripolyphosphate consists of calcination or dissolution of sodium phosphates or sodium pyrophosphates.

MATERIALS

One type of commercial sodium tripolyphosphates was characterized in the present work, supplied by two different companies that market this product and sell it to the main Brazilian ceramic industries. These sodium tripolyphosphates were referenced TPF 1 y TPF 2.

To determine the deflocculating capacity of the sodium tripolyphosphates, a characterized kaolin suspension prepared with 60% solids content was used.

DISCUSSION AND RESULTS

Table 1 shows the chemical analysis of the two types of sodium tripolyphosphate and it can be observed that significant differences exist between the ion quantity that the STPs form, with a given quantity of Al_2O_3, which for sample type 1 is almost double that of sample type 2.

Using the table, it is possible to calculate the P_2O_5/ Na_2O ratio, because through the periodic table, the molecular weight of $3P_2O_5$/ $5Na_2O$=1.37 is calculated, and this value is utilized as the theoretical ratio of phosphorus and sodium in the sodium tripolyphosphate.

The P_2O_5 / Na_2O ratio for TPF1 is 1.69 and for TPF2 is 1.42, which is closer to the theoretical value, so that TPF1 presents a P_2O_5 / Na_2O ratio about 17% higher than TPF2, due to the fact that TPF1 can be formed by long chain sodium polyphosphates with a higher P_2O_5 / Na_2O mass ratio, or can contain other phosphates of a higher P_2O_5 / Na_2O mass ratio besides sodium tripolyphosphates.

As both differ from the theoretical value (1.69) and are quite different from each other, their efficiency as deflocculants tends to be very different, because some ions present in the STPs act as flocculants in the suspensions, disturbing the dispersion, for example, as happens with aluminium.

Compound	TPF 1	TPF 2
Al_2O_3	0.088	0.045
CaO	0.014	0.024
Fe_2O_3	0.035	0.029
K_2O	0.055	0.064
MnO	>0.01	0.013
Na_2O	37.24	41.680
P_2O_5	62.984	59.158
SiO_2	0.221	0.131
TiO	Not detected	Not detected
MgO	>0.1	Not detected

Table 1- Chemical analysis of sodium tripolyphosphates.

As a proposal to improve the STP effectiveness, a hydration was performed according to the method described above and to verify whether the hydration method was efficient or not, X-ray diffraction was carried out, as shown by figures 1 and 2. This was carried out for the two samples, however as the results are identical, only the results for TPF1 are shown. Figure 1 shows only the anhydrous crystalline phase of the STP and figure 2 presents only the hexahydrated form of the STP, which confirm that the proposed hydration method is efficient.

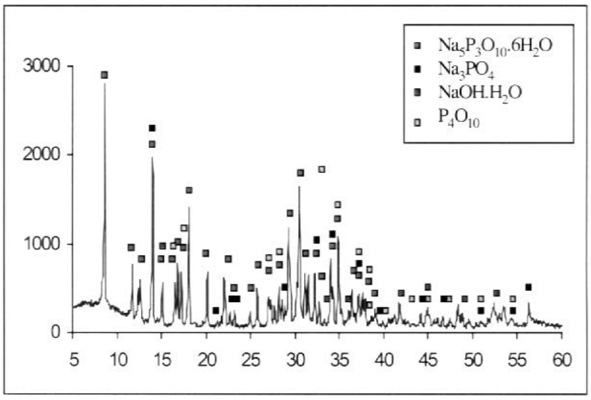

Figure 1- TPF before hydration, in natura.

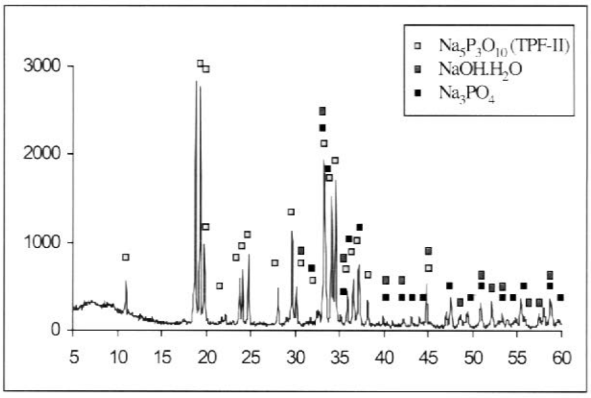

Figure 2- TPF after hydration.

To verify deflocculation effectiveness, the curves were obtained of both products *in natura* according to figure 3 and hydrated, according figure 4. Figures 5 and 6 present the evolution of viscosity vs the STP1 and STP2 % *in natura* and hydrated.

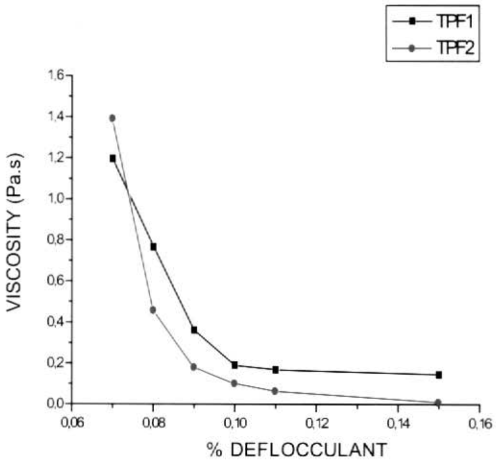

Figure 3 – Evolution of viscosity vs STP% in natura.

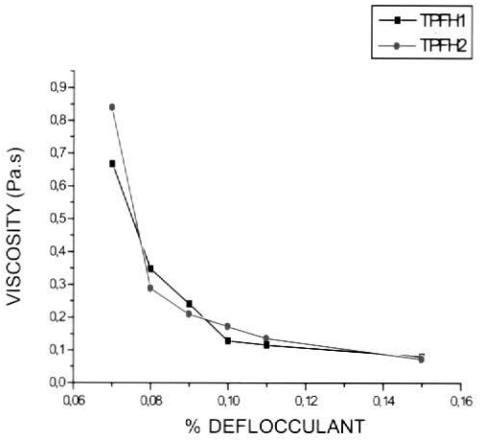

Figure 4 – Evolution of viscosity vs STP% hydrated.

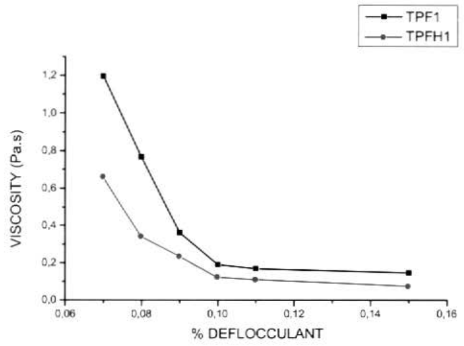

Figure 5 – Evolution of viscosity vs STP1 % in natura and hydrated.

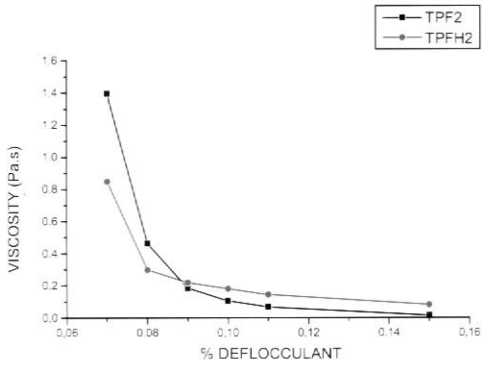

Figure 6 – Evolution of viscosity vs STP2 % in natura and hydrated.

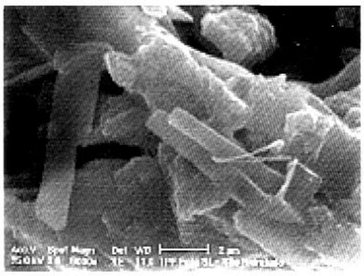

Figure 7 – Micrograph of non-hydrated STP.

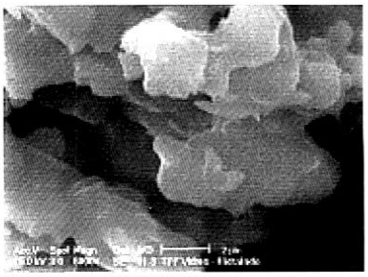

Figure 8 – Micrograph of hydrated STP.

CONCLUSION

The hydration of sodium tripolyphosphate is a simple method and highly efficient, not requiring the utilization of CMC as an additive to help the deflocculation.

The impurities that can be found do not significantly influence in its dispersing capacity.

There are sodium tripolyphosphates in the market with lots of impurities, which are sold to other sectors of the market, such as detergent industries. For this reason, they have lower prices compared to those offered to the ceramic industries. However, with hydration these sodium tripolyphosphates can be utilized, producing savings in the price of this raw material, and the cost with water can be compensated with the water that is already utilized in the slips and glaze mills, without increasing costs and keeping ideal viscosity and density of the mixture, not changing the process.

The micrograph with 6000X magnification clearly shows the differences between the non-hydrated and hydrated particles, which give rise to the differences in their properties.

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