



# Stabilization of raw porcelain gres suspensions with sodium naphthalene sulfonate formaldehyde condensates

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## ABSTRACT

The stabilization of raw porcelain gres suspensions with sodium naphthalene sulfonate formaldehyde condensates (SNSFC) was examined systematically in order to understand the basis mechanism of dispersion. Small additions of SNSFC to the classical deflocculating mixture with sodium silicate were tested. The repulsion between the colloidal particles was correlated with the adsorption isotherm and zeta potential. The naphthalene sulfonate condensates were effective as dispersant for raw porcelain gres suspensions. The efficiency of these dispersant was attributed to electrostatic effect between the colloidal particles. The ability of the SNSFC to stabilize raw porcelain gres suspensions was not affected by the degree of condensation.

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## 1. Introduction

Within the great range of products offered by the ceramic industry, developments in porcelain tile commonly referred to as porcelain gres, have been outstanding. During the past five years, the production has increased currently accounting for 40% of European's total product output. As the demand for porcelain gres continues to increase, leading edge techniques will be required to assist manufacturers in improving their products. Some processing techniques, for example slip casting or injection moulding, use ceramic suspensions with high solid volume and proper stability to improve its economics [Tobori and Amari, 2003]. However, with increasing solid loading, processing of a suspension becomes increasingly difficult. Since its flow characteristics are usually of crucial importance, they have to be controlled in order to yield a final product with the best properties as well as to improve the economics of the process to optimize energy requirements [Papo et al., 2002]. In general, controlling viscosity and adequate stability of concentrated suspensions is an essential part of successful porcelain powder processing. This stability is produced by the interaction of moving porcelain particles within the interparticle fluid [Bergström, 1998]. In general, it is strongly affected not only by solid loading, but also by chemical aspects, i.e. of pH and/or addition of dispersing agents.

Dispersing agents based on polyelectrolytes, such as polyacrylates, polysaccharides and polystyrene sulfonates, have been used in the preparation of these concentrated suspensions [Tadros, 1980]. The purpose of this paper is to investigate the stability of concentrated suspensions of raw porcelain particles in the presence of different sodium naphthalene

sulfonate formaldehyde condensate by comparing with the classical and economical deflocculating mixture with sodium acrylate (SA) and sodium silicate [Manfredini et al., 1987; Sheppard, 1990].

Naphthalene sulfonate formaldehyde condensates are used in a number of consumer products and industrial processes that involve particles of a colloidal nature. Examples of such applications are as diverse as cement production, pigment and dyestuff formulation, elastomer manufacture, agrochemicals, haircare products, textiles and mineral processing [Huynh et al., 2001]. Despite their commercial importance, a surprising paucity of studies involving SNSFC exists in the literature. In general, the few studies that have been reported have focussed on adsorption of the SNSFC molecules at the solid surface-solution interface [Kim et al., 1995]. A few investigations [Marco and Llorens, 2007] have used settling tests to assess the effect of SNSFC on dispersion stability. However, to the best of our knowledge, there have been no earlier studies that have attempted to elucidate the effect of naphthalene sulfonate formaldehyde condensate adsorption on the interaction forces between porcelain gres particles. This will be achieved through correlation of adsorption, electrokinetic and rheological data. In this context this study relates the adsorption density of polymer onto the surface of porcelain gres and the electrostatic and steric forces [Zaman et al., 2002]. Rheological measurements have been used for the evaluation of the fluidity of powder suspensions [Snabre and Mills, 1999].

## 2. Experimental procedure

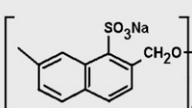
### 2.1. Materials

The basic composition of the raw porcelain gres material was a synthetic mixture supplied by ECESA (Lugo, Spain) whose mineralogical

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**Table 1**  
Chemical structure and properties of polyelectrolytes

Polymer	Chemical Structure
Sodium acrylate homopolymer (SA). MW = 2000g mol <sup>-1</sup> Max. polymer charge density (pH=8) = 1026C/g	$\left( -\text{CH}_2-\underset{\text{O}^-\text{C}-\text{O}^-}{\text{CH}}- \right)$ Na <sup>+</sup>
Sodium salt of copolymer of naphthalene sulfonated (SNSFC). MW(monomer) = 258g mol <sup>-1</sup> SNSFC <sub>1</sub> -Degree of condensation = 3 SNSFC <sub>2</sub> -Degree of condensation = 5 SNSFC <sub>3</sub> -Degree of condensation = 7 Max. polymer charge density (pH=8) = 374 C/g	

composition was 45 wt.% feldspar, as fusion agent, 40 wt.% plastic clay, as plasticizing agent, and 15 wt.% kaolin, as whiting agent. The mean diameter of the raw porcelain gres particles, measured by laser diffraction (LD), was 2.5  $\mu\text{m}$  and with about 100% of the material below 3–4  $\mu\text{m}$  and the 50% of the ceramic particle was over than 1  $\mu\text{m}$ . The specific surface area for this powder was 16.9  $\text{m}^2 \text{g}^{-1}$ , determined by nitrogen adsorption (BET). The isoelectric point (IEP) was at pH 9.0, determined by acid–base titration [Arias et al., 1995]. Two different chemical additives have been evaluated, one is a linear homopolymer of sodium acrylate (SA), used in the ceramic industry as a classical mixture with sodium silicate and, the other is a condensate of sodium naphthalene sulfonate (SNSFC), used in the concrete industry as superplasticizer. A series of three different condensates, SNSFC<sub>1</sub>, SNSFC<sub>2</sub> and SNSFC<sub>3</sub>, has been tested in order to study the effect of the degree of condensation on the stabilization. Some physical properties and the chemical structures of these dispersants are given in Table 1. The polymers based on sodium acrylate, SA, have been supplied by Rohm and Haas Company, whereas the three different SNSFC have been provided by Dalton S.P.A. The infrared spectrum of the used SNSFC is presented in Fig. 1. The infrared spectrum contains the aromatic C–H stretch band at 3070  $\text{cm}^{-1}$ , the aromatic ring modes at 1640, 1596 and 1507  $\text{cm}^{-1}$  and the sulfonate group bands at 1190, and 1033  $\text{cm}^{-1}$ . Additionally, the spectrum contains the methylene C–H bending (scissors) vibration at 1460  $\text{cm}^{-1}$ . All the naphthalene sulfonate formaldehyde condensates have almost the same spectrum.

All tested deflocculant mixtures contained 25 wt.% of commercial polymer with a solid content of 50 wt.% and a 75 wt.% of sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O}=1$ ) supplied by FMC Foret Corporation. This is a typical formulation used by ceramic suspension manufacturers where the polyelectrolyte is the main ingredient and sodium silicate acts as coadjuvant [Collepardi, 1998].

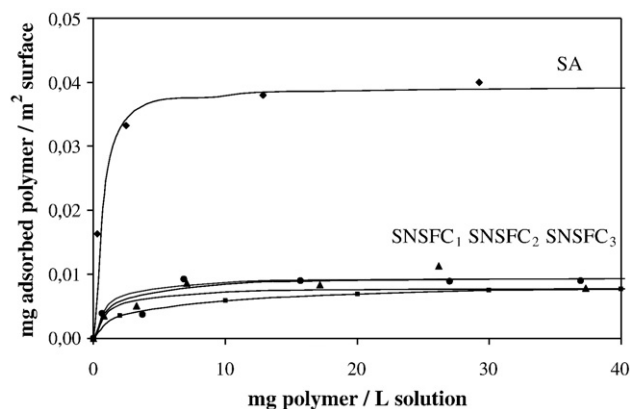


Fig. 2. Adsorption isotherms: SA (◆), SNSFC<sub>1</sub> (▲), SNSFC<sub>2</sub> (■) and SNSFC<sub>3</sub> (●).

## 2.2. Methods

### 2.2.1. Adsorption isotherms

Ceramic dispersions were prepared by mixing 1 g of the raw material with 50 mL of polymeric solution, without the sodium silicate. A total of 24 different dispersions were prepared by adding the four different polymers at six different concentrations: 0, 2, 10, 20, 30 and 40  $\text{mg L}^{-1}$ . The natural pH of the solutions was around 8. The mixture was stirred overnight. After equilibration took place, the mixture was centrifuged. The settled dispersion was filtrated with a 0.2  $\mu\text{m}$  cellulose microfilter. The polymer concentration of SA in the filtered solution was determined by the Nephelometric Method using a UV/VIS Lambda 20 (Perkin Elmer, United States) spectrophotometer. The amount of free polymers of SNSFC in the clear layer was measured by UV spectrophotometry at 290 nm.

The amount of polymer adsorbed on the particles was evaluated from the difference between the initial polymer concentration and the polymer concentration in the supernatant.

### 2.2.2. Electrophoretic measurements

The specific polymeric electrical charge was determined from the measurement of zeta potential. This measure was evaluated by electrophoresis. A diluted porcelain gres suspension was preparing prepared by dispersing 0.1 g of porcelain gres in 100 mL of solution. A total of 20 different polymer solutions were prepared by adding the four different polymers at five different concentrations: 0, 50, 100, 200 and 250  $\text{mg L}^{-1}$ . A ZetaSizer instrument (ZetaSizer Nano ZS, Malvern Instruments INC., United Kingdom) was used to evaluate the dynamic mobility [Ribitsch et al., 1988]. The zeta potential,  $\zeta$ , was calculated

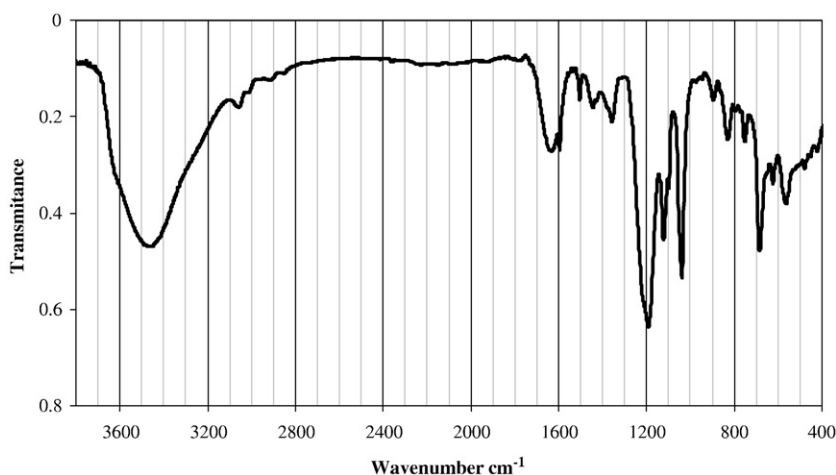


Fig. 1. Infrared spectrum of SNSFC.

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