SUBSTITUTION OF RAW MATERIALS IN AN INDUSTRIAL POROUS SINGLE FIRED PRODUCT

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ABSTRACT

Different amounts of polishing sludges were used to prepare ceramic mixes for porous single fired tiles, as partial substitutions of some of the natural raw materials. With the aim to optimise the recycling process, the sludges were first of all characterized to determine their chemical and mineralogical composition. Then, the rheological behaviour of the corresponding concentrated suspensions was studied by using a rotational rheometer. The effect of the dispersant was also evaluated.

1. INTRODUCTION

In the last years a lot of studies were carried out to implement the reuse of some industrial wastes[1] or bottom ash in new ceramic products, as in some cases wastes can be considered new resources to substitute expensive raw materials[2]. Due to the large consumption of mineral resources in the ceramic industry, a closed loop recycling of ceramic wastes may have beneficial environmental and economical impacts and it could be favoured by the compositional similarities with ceramic product. In the porcelain stoneware production, various surface treatments are applied to achieve innovative effects, such as polishing and satin finishing. The industrial polishing process involves the use of a succession of polishing stages with steadily decreasing abrasive particle size and originates a lot of sludges. The polishing sludges are composed by water and very fine debris coming from the tiles and the tools bond, rich in magnesium carbide, and abrasive particles driven out from the tools. These wastes are classified as non-hazardous and, after removing water, are generally disposed in landfill sites. Chemically the polishing sludges are composed by a relevant presence of silica and alumina and not negligible amounts of alkaline and alkaline earth oxides that may influence the rheology of the slurry of the ceramic product. Therefore, to recycle this kind of waste, it is necessary to optimise the body mix formulation. From the rheological point of view, it is important to define the ideal amount of sludges to add in a ceramic mix in order to obtain a stable suspension.

2. MATERIALS AND METHODS

A body for porous single fired tiles, denoted as MPST, has been selected as reference material. Their composition, in terms of raw materials, is reported in table 1. The chemical compositions of the polishing sludges were performed by inductively coupled plasma emission (ICP 3200XL Perkin Elmer, USA). Five porous single fired mixes were prepared by replacing the flux 1 or the sand 2 with different percentages of sludges (table 1). The effect of deflocculant was tested also and some slips were prepared by using different deflocculant amounts. The porous single fired raw materials were dispersed in water (35 wt.%) with a dispersant (Daxel), a sodium silicate, and milled in a jar for 1h.

Raw Materials	MPST (wt.%)	MP ST5L (wt.%)	MP ST8L (wt.%)	MP ST5Lsab (wt.%)	MP ST8Lsab (wt.%)	MP ST5L0.9 (wt.%)
Clay 1+ Clay 2	49.0	49.0	49.0	49.0	49.0	49.0
Flux 1	11.5	6.5	3.5	11.5	11.5	6.5
Sand 2	11.0	11.0	11.0	6.0	3.0	11.0
Sludges	---	5.0	8.0	5.0	8.0	5.0
Dispersant	0.7	0.7	0.7	0.7	0.7	0.9
Carbonates (5.5 wt%), Chamotte (8.0%) and sand 1 (15%) percentages remain constant.						

Table 1. Formulations of porous single fired mixes

3. RESULTS

The viscoelastic behaviour of suspensions is usually evaluated by the oscillatory tests. These tests consist of applying a small amplitude3 sinusoidal oscillation to a viscoelastic material and the resulting stress is compared with the strain. From the oscillation curves it is possible to obtain information about the stability and the structure of suspension4. This kind of measurement is not destructive since the applied strain is very low. The ceramic suspensions typically show the elastic response (G′) exceeding the viscous one (G′′) as these systems exhibit a Kelvin solid like behaviour.

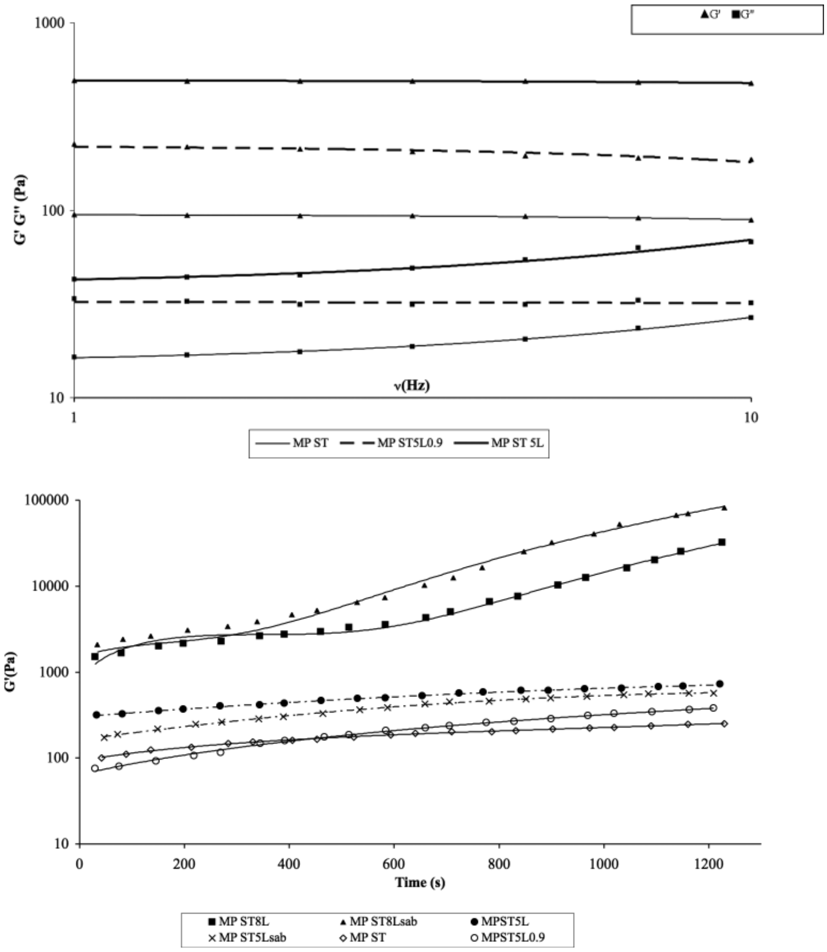

Figure 1: a) dynamic measurements for samples at two different deflocculant contents to evaluate moduli as a function of frequency; b) Moduli of samples with different additions and deflocculant concentrations as a function of time

The moduli of a stable suspension increase with the frequency while coagulated or structured suspensions show constant moduli (G′ and G′′) with the frequency. The porous single fired mix without the sludges addition, MPST, exhibits a solid-like behaviour (fig. 1a); when wastes are added the behaviour does not change but the elastic modulus increases and this can be expected as the instability of the slurry becomes more important. In fig. 1b the time dependency effects are shown. The kinetic of build up is represented by the increment of G′ with the time when 8% of sludges is added. By increasing the deflocculant amount it is possible to reduce the structuration effects of the sludges addition due to the presence of Mg^{2+} which increases in the presence of sludges (from 0.3wt% to 0.6wt%). In figs. 1a and b it is clear that the modulus decreases in presence of a greater quantity of deflocculant and it remains constant with the time. The presence of magnesium was demonstrated[5] to have some effects of compressibility of the double layer leading to the coagulation of the dispersion. Another important aspect to underline is the particle size. Sludges exhibit very fine particle size (table 2) so that when added at the suspensions, the surface area increases and a higher amount of deflocculant is necessary.

	d(10) (μm)	d(50) (μm)	d(90) (μm)
Sludges	2.14	12.25	41.27
Flux 1	13.75	79.00	164.41
Sand 2	4.75	50.79	140.26

Table 2. Particle size of raw materials.

4. CONCLUSIONS

In the case of porous single fired mix, the amount of recyclable polishing sludges should be lower than 5 wt.%, Two different aspects of the slips destabilisations are observed: i) the presence of bigger and more charged ions, such as Mg^{2+}, that modifying the double layer thickness favour coagulation effects; ii) the very fine particle sizes of the sludges, which increases the surface area of the solid content in the slips. To stabilise such kind of suspension a large deflocculant content is required.

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