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SUBSTITUTION OF RAW MATERIALS IN DIFFERENT CERAMIC INDUSTRIAL PRODUCTS

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ABSTRACT

Different amounts of polishing sludges were used to prepare ceramic mixes for porcelain stoneware and 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. The different behaviour among all the samples was correlated to their different chemical compositions, in particular in terms of alkali and alkali earth ions.

1. Introduction

In the last years a lot of studies were carried out to implement the reuse of some industrial wastes¹ or bottom ash² in new ceramic products, as in some cases wastes can be considered new resources to substitute expensive raw materials^{3,4}. Due to the large consumption of mineral resources in the ceramic industry⁵, a close loop recycling of ceramic wastes may have beneficial environmental and economical impacts and it could be favored by the compositional similarities with ceramic product. Several wastes, such as cement, bricks or tiles, have been identified for possible incorporation in ceramic products⁵. 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 and the sintering conditions 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, by controlling the presence of those ions, such as Mg, Ca, which tend to aggregate the particles. The stability of the ceramic slurries may be compromised also by the very fine particle sizes of the sludges. At this purpose, a rheological study allows to define the optimal percentage of deflocculant to insert in the ceramic mixes. In this paper several percentages of polishing sludges were introduced in two different ceramic mixes, a porcelain stoneware and a white porous single fired ("monoporosa") mixes, in partial substitution of some of the natural raw materials. Porcelain stoneware represents an advanced product among all the typologies of ceramic tiles, being characterized by a very low water absorption, lower than 0.5wt.%, while the porous single fired is a wall tile, generally glazed, with values water absorption higher than 10wt.% (EN ISO 10545-3). The aim of this work is to optimize, in particular in terms of rheology, the recycling of polishing sludges in the ceramic tiles, studying the physical-chemical interactions and the instability phenomena caused by their presence.

2. Materials and methods

Two ceramic bodies for porcelain stoneware and porous single fired tiles, denoted as ST and MPST, respectively, have been selected as reference materials. Their composition, in terms of raw materials, is reported in tables 1 and 2. The chemical and mineralogical compositions of the polishing sludges were performed by inductively coupled plasma emission (ICP 3200XL Perkin Elmer, USA) and X-ray diffraction analysis (PW3830, Philips, NL) and are reported in table 3.

Table 1: Formulations of porcelain stoneware mixes

Raw materials	ST (wt.%)	ST5 (wt.%)	ST7.5 (wt.%)	ST10 (wt.%)	ST15 (wt.%)	ST15-0.8 (wt.%)	ST15-1.0 (wt.%)
Clay U	32.9	32.9	32.9	32.9	32.9	32.9	32.9
Clay	10.1	10.1	10.1	10.1	10.1	10.1	10.1
Chamotte	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Feldspar T	31.1	26.1	23.6	21.1	16.1	16.1	16.1
K-feldspar	6.6	6.6	6.6	6.6	6.6	6.6	6.6
Sand K-feldspar	12.3	12.3	12.3	12.3	12.3	12.3	12.3
Sludges	32.9	5.0	7.5	10.0	15.0	15.0	15.0
Dispersant	0.6	0.6	0.6	0.6	0.6	0.8	1.0

Six porcelain stoneware mixes were prepared by substituting the feldspar T with different amounts sludges, as reported in table 1, and five porous single fired mixes were prepared by replacing the flux 1 or the sand 2 with different percentages of sludges (table 2). The effect of deflocculant was tested also and some slips were prepared by using different deflocculant amounts (tables 1 and 2). In table 3 the chemical compositions of the partially replaced natural raw materials are also reported. The porcelain stoneware mixes were obtained by dispersing the raw materials in water (33wt.%) with a dispersant (Fluicer CF907), a mix of sodium silicate and sodium polyphosphate, and milling in a jar for 1h. The porous single fired raw materials were dispersed in water (35wt.%) with a dispersant (Daxel), a sodium silicate, and milled in a jar for 1h.

Table 2: Formulations of porous single fired mixes

Raw Materials	MPST (wt.%)	MP ST5L (wt.%)	MP ST8L (wt.%)	MP ST5Lsab (wt.%)	MP ST8Lsab (wt.%)	MP ST5L0.9 (wt.%)
Clay 1	24.0	24.0	24.0	24.0	24.0	24.0
Clay 2	25.0	25.0	25.0	25.0	25.0	25.0
Carbonates	5.5	5.5	5.5	5.5	5.5	5.5
Flux 1	11.5	6.5	3.5	11.5	11.5	6.5
Sand 1	15.0	15.0	15.0	15.0	15.0	15.0
Sand 2	11.0	11.0	11.0	6.0	3.0	11.0
Chamotte	8.0	8.0	8.0	8.0	8.0	8.0
Sludges	---	5.0	8.0	5.0	8.0	5.0
Dispersant	0.7	0.7	0.7	0.7	0.7	0.9

To obtain powders suitable for shaping, all the slurries were dried at 110°C for 12h, crushed and sieved to pass at 125µm screen. Specimens, in form of disks (40mm of diameter) were prepared by wetting (about 6%), then sieving (to eliminate agglomerates) the powders and, finally, pressing at 30 MPa the porous single fired mix and at 52MPa the porcelain stoneware mix. The disks were then sintered in a laboratory gradient furnace (Ceramic Instrument mod. 86/V).

Table 3: Mineralogical composition of sludges and substituted raw materials.

	Cristalline phases
Sludges	Quartz, Zircon, Na-K Feldspar, Mullite, Calcite, Magnesite, SiC
Feldspar T	Quartz, Na-Ca Feldspar
Flux 1	Quartz, Na-K Feldspar, Illite

Table 4: Rheological data of porcelain stoneware mixes

Sample	pH	ρ (kg/m ³)	η (5s ⁻¹) (Pa s)	η (50s ⁻¹) (Pa·s)	Model parameters		
					τ_o (Pa)	η_p (Pa s)	r
ST	8.78	1725	0.62	0.23	0.1	0.19	1.000
ST5	8.89	1722	0.33	0.27	1.0	0.27	0.998
ST7.5	8.89	1720	0.76	0.30	1.1	0.31	0.997
ST10	8.59	1696	0.49	0.70	0.4	0.29	0.998
ST15	8.67	1716	1.48	0.86	5.2	0.42	0.997
ST15-0.8	8.68	1715	0.83	0.56	1.3	0.38	0.997
ST15-1.0	9.23	1720	0.94	0.48	5.9	0.38	0.995

Table 5: Rheological data of porous single fired mixes

Sample	pH	ρ (kg/m ³)	η (5s ⁻¹) (Pa.s)	η (50s ⁻¹) (Pa.s)	Model parameters		
					τ_o (Pa)	η_p (Pa s)	r
MP ST	9.07	1760	13.5	1.93	50.87	0.53	0.98
MP ST5L	8.90	1680	19.6	2.35	67.54	0.65	0.99
MP ST8L	8.90	1680	17.4	2.8	103.6	0.57	0.99
MP ST5Lsab	9.05	1720	13.4	1.78	90.25	0.28	0.97
MP ST8Lsab	9.11	1730	-----	-----	-----	-----	-----
MP ST5L0.9	8.95	1678	9.85	1.99	31.05	0.68	0.99

The porcelain stoneware and the porous single fired samples were sintered at different maximum temperatures depending on the compositions. The porcelain stoneware mixes were sintered until 1250°C for a total time of 1h 50' while the porous single fired mixes were sintered until 1180°C for a total time of 1h and 28'.

The sintering behaviour of the fired specimens was evaluated on the basis of their linear shrinkage and water absorption, determined according to the test method recommended for ceramic tiles, reported in the Standard EN ISO 10545-3.

A rheological characterisation on the suspensions is fundamental in order to verify the right amount of deflocculant and sludges. A rotational rheometer RS50 Haake (Germany) equipped by plate-plate and cone-plate sensors, PP60 (plate-plate) for steady state measurements and DC60/2° (cone-plate) for oscillatory tests, was used. The shear behaviour was evaluated by a flow curve in control rate mode between 0 s⁻¹ and 50 s⁻¹. A control stress flow curve in the range 0 Pa to 50 Pa, in 300s was performed to evaluate the yield stress^{6,7}. Dynamic measurements of frequency sweep were performed in the linear viscoelasticity region between 0.1Hz and 10Hz.

Table 6: Alkalis content of studied mixes.

Samples	CaO (wt.%)	MgO (wt.%)	K ₂ O (wt.%)	Na ₂ O (wt.%)
ST	0.7	0.3	1.9	3.5
ST5	0.7	0.5	1.9	3.3
ST10	0.7	0.7	2.0	3.1
ST15	0.7	0.9	2.1	2.8
MP ST	3.5	0.3	2.3	1.8
MP ST5L	3.6	0.5	2.4	1.6
MP ST8L	3.6	0.6	2.4	1.4
MP ST5Lsab	3.6	0.5	2.2	2.0

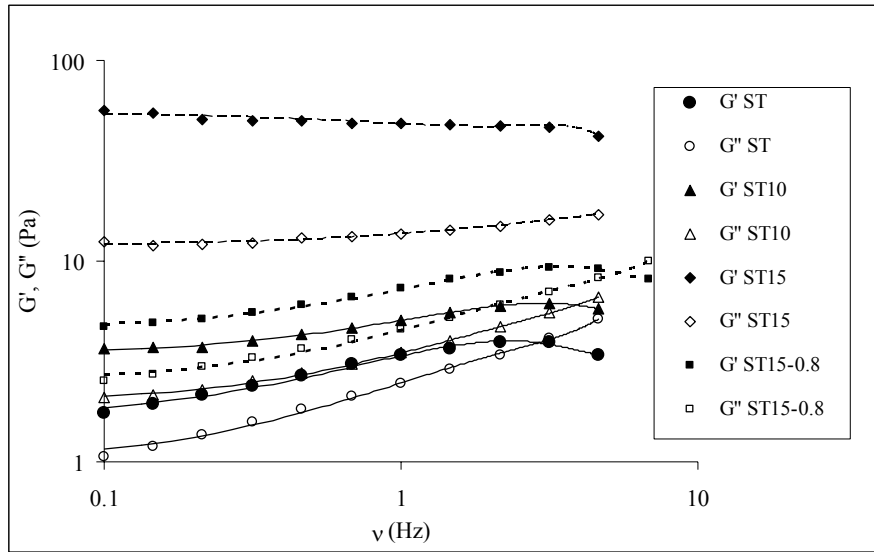


Figure 1: Dynamic measurements to evaluate moduli in the function of frequency for the porcelain stoneware mixes.

The viscoelastic behaviour of suspensions is usually evaluated by the oscillatory tests. These tests consist of applying a small amplitude 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 suspension. This kind of measurement is not destructive since the applied strain is very low.

The oscillation tests are usually performed by small strains⁸ to assure to operate in the linear viscoelastic region where the values of moduli do not change with the applied stress and the interdependence between strain and stress is linear. This region depends on the material structure, in particular in terms of particles mutual interactions which depend on the attractive and repulsive forces able to stabilise the system. The linear range is a function of the type of interactions among the particles and the shape of them also⁹. The oscillatory measurements were performed in order to study the effects of the waste contents on the suspensions stability. The influence of sludges concentration on the storage and elastic modulus were studied in the function of the time in order to evaluate the time effects on the slurries.

The linear viscoelastic region was determined by performing rheological measurements as a function of the strain amplitude at a fixed frequency (1Hz). In this region, G^* (complex modulus), G' (elastic modulus) and G'' (viscous modulus) are independent on strain at any given frequency^{10,11}.

$$G^* = \tau_0/\gamma_0 = G' + iG'' \quad \text{with} \quad G' = G^* \cos \delta \quad G'' = G^* \sin \delta \quad \text{and} \quad \tan \delta = G''/G' \quad (1)$$

Measurements were then carried out as a function of frequency and at a fixed amplitude corresponding to the linear region. The frequency range tested was between 0.1 and 10 Hz.

3. Results

The rheological results for the porcelain stoneware and the porous single fired suspensions are reported in tables 4 and 5, respectively. The rheological parameters were elaborated by the Bingham model, eq.2, where τ_0 is the yield stress, η is the viscosity and $d\gamma/dt$ is the shear rate. In the case of porcelain stoneware slips, a more relevant amount of sludges it are added, respect to the porous single fired ones, for which a rather low sludges concentration is maintained. The addition of the polishing waste in porcelain stoneware mixes changes the charge distribution of the suspensions because of the presence of higher amounts of the rather big and charged ions in the sludges, such as magnesium ions, as indicated in table 6. The macroscopic effect of this phenomena is an increment of aggregation among the particles and a viscosity growth. In fact, magnesium ions are able to increase the viscosity, by modifying the ζ -potential and, consequently, the mechanism of the dispersant action. With the 15% of sludges in the porcelain stoneware mix, ST15, a drastic increasing of the yield stress and viscosity is achieved. By increasing the deflocculant concentration from 0.6wt.% to 0.8 wt.%, ST15-08, the yield stress, in particular, and the viscosity decrease immediately (table 4). On the contrary, a higher addition of dispersant, 1wt.%, ST15-1.0, causes an increasing of the experimental viscosity (at 5 and 50 s⁻¹) and the yield stress, respect to ST15 mix, with 0.6wt.% of deflocculant.

$$\tau = \eta \, d\gamma / dt + \tau_0 \quad (2)$$

In the case of porous single fired mixes, to reduce the yield stress, it is necessary to increase the amount of dispersant until 0.9wt.%, MPST5L09, (table 5). The structuration effect due to the presence of sludges is confirmed by the oscillatory tests. The real suspensions behaviour reflects an intermediate behaviour between the perfect elastic system and the viscous one. The concentrated suspensions exhibit generally viscoelastic behaviour as they show a simultaneous elastic and viscous response. The elastic contribution is represented by the Newtonian law and the viscous one by the Hooke law.

Table 7: Particle size of raw materials, in term of percentiles (d).

	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

The real viscoelastic suspensions can be described through two ideal models: the solid-like model of Kelvin and the viscoelastic liquid model of Maxwell. In the first model the strains are reversible, elastic but not instantaneous, while in the second one, the total strain is the sum of a reversible, instantaneous elastic strain and a permanent time-dependent viscous component. So, in general, diluted suspension or well dispersed slurry exhibits a behaviour *Maxwell like*, in which G'' (loss modulus) exceeds the elastic response (G' , storage modulus). The ceramic suspensions show typically the elastic response exceeding the viscous one as these systems exhibit a *Kelvin solid like* behaviour. The moduli of a

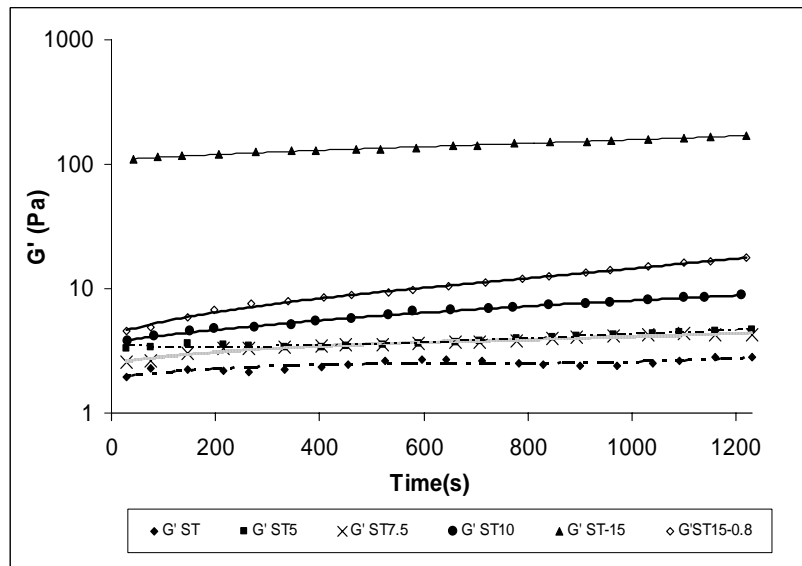
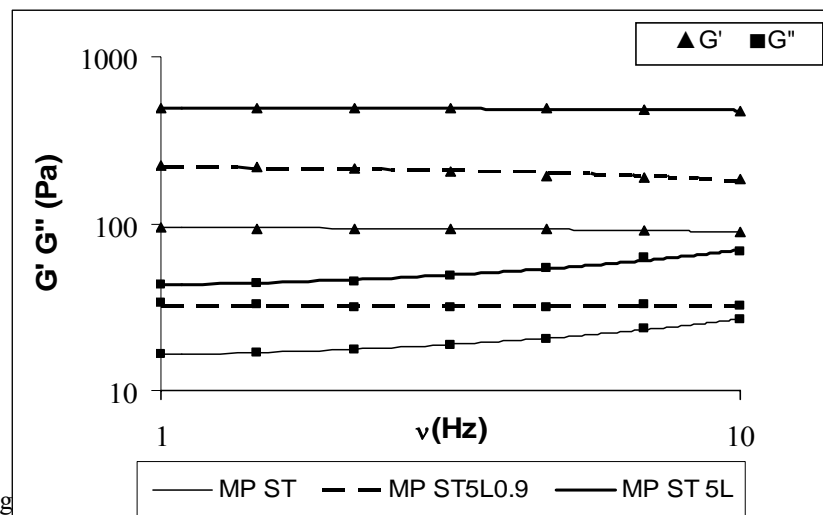


Figure 2: Moduli of porcelain stoneware mixes in function of the time.

stable suspension increase with the frequency while coagulated or structured suspensions show constant moduli (G' and G'') with the frequency. The porous single fired samples exhibit this behaviour. The dynamic measurements show an increment of instability due to the presence of the sludges, in fact a change of the elastic modulus can be observed in fig. 1 that shows a typical gel like behaviour in the sample with the highest percentage of sludges. To obtain a liquid like behaviour it is necessary to add more deflocculant. In fig. 2 the trend of G' with the time confirms that the building



Fig

up phenomena decreases in presence of a great percentage of deflocculant. The porous single fired mix without the sludges addition, MPST, exhibits a solid like behaviour (fig. 3); 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

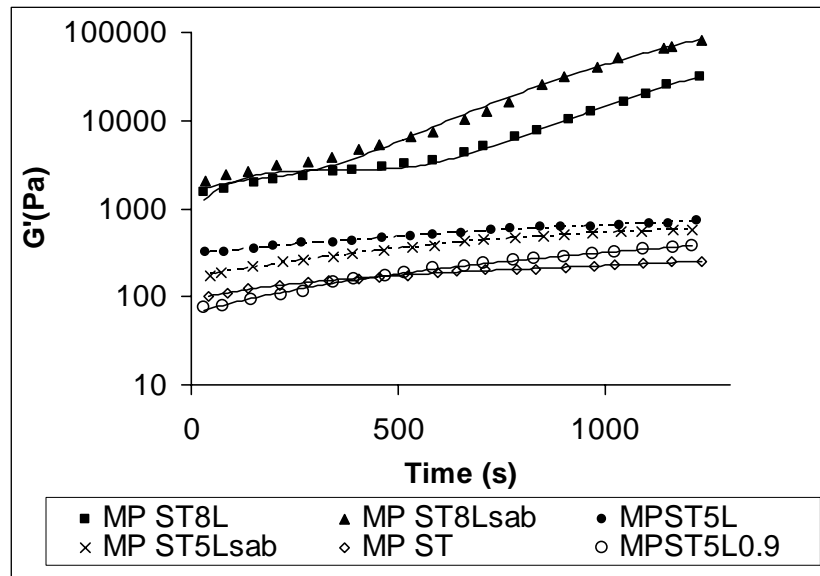


Figure 2: Moduli of porous single fired mixes in function of the time

In fig. 4 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. In figs. 3 and 4 it is clear that the modulus decreases in the presence of a greater quantity of deflocculant and it remains constant with the time. The presence of magnesium was demonstrated to have some effects of compressibility of the double layer leading to the coagulation of dispersion^{12,13}. In the table 6 the alkalis content is reported and it can be evidenced that magnesium oxide tends to increase with sludges content. An other important aspect to analyse is the particle size. Sludges exhibit very fine particle size (table 7) so that when added at the suspensions, the surface area increases and a higher amount of deflocculant is necessary. In the tables 8 and 9, firing results are reported and it can be evidenced as the presence of sludges in the porcelain stoneware mix allows to sinter at lower temperature so sludges show a strong fluxing effect. By the way the shrinkage is not so constant at the maximum temperature. The porous single fired samples shows a firing behaviour which does not seem to be influenced by the presence of sludges. Increasing the waste addition, only a low reduction of water absorption is observed at the same firing temperature.

Table 8: sintering data of porcelain stoneware samples

Sample	Temperature (°C)	Shrinkage (%)	Water absorption (wt.%)
ST	1230	8.8	0.00
	1250	8.5	0.00
ST5	1230	7.1	0.00
	1250	5.0	0.00
ST7.5	1190	7.1	0.00
	1210	5.0	0.00
ST10	1210	9.2	0.00
	1230	8.7	0.00
ST15	1170	8.0	0.50
	1190	1.2	0.00

Table 9: sintering data of porous single fired samples

Sample	Temperature (°C)	Shrinkage (%)	Water absorption (wt.%)
MPST	1160	1.0	16.92
	1180	2.2	14.63
MPST5L	1160	1.6	15.98
	1180	3.5	11.54
MPST8L	1160	1.0	16.88
	1180	4.4	13.30

It is interesting to evidence that the addition of waste can cause more problems in the porous single fired mixes than in the porcelain stoneware ones. In the porous single fired mixes it is possible to introduce a rather low quantity of wastes, lower than 5wt.%, while in the case of porcelain stoneware the percentage of addition can reach 10wt.% or more.

The modified porcelain stoneware samples, containing the polishing sludges, exhibit 0wt.% of water absorption at lower temperatures than the standard composition, as reported in the table 9. So the waste material plays a positive role on the sintering behaviour, even if the shrinkage is not so constant at high temperatures.

The waste addition in the porous single fired samples does not change significantly the sintering behaviour respect to the standard material.

4. Conclusions

The introduction of a waste in a ceramic mix is subordinated to the nature of the mix. In this paper it is evidenced that the porcelain stoneware can be the best material to recycle polishing sludges. This is due to the particular nature of this waste which is very similar to the mix so that the percentage of recyclable sludges can reach 10-15wt.%. But it is important to evidence that, as the porcelain stoneware suspensions are quite stable, it is necessary to introduce a high quantity of big and charged ions like Mg^{2+} , to change the electrical stability of the slurry. For the porcelain stoneware, some problems may occur during the sintering process as the introduction of sludges causes a dimensional instability of the final product. In the case of porous single fired mix, the amount of recyclable sludges are lower, only 5wt.%, and two different aspects of destabilisations are observed. When sand or flux are substituted by the sludges, yield stress and viscosity are strongly influenced. The presence of bigger and more charged ions, modifies the double layer thickness and the coagulation effects are increased. Another effect is due to the very fine particle sizes of the sludges, that tends to increase the surface area. Therefore to stabilise the suspension a great deflocculant content is needed. The crucial problem is to find the conditions to stabilise the suspension., whereas the sintering process does not change significantly and the shrinkage and water absorption values remain rather constant (water absorption 14-16 wt.%).

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