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"SANITSER", AN INNOVATIVE SANITARYWARE BODY, FORMULATED WITH WASTE GLASS AND RECYCLED MATERIALS.

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Abstract

In the present paper we present the results of "Sanitser" Life European project. In this latter we worked with the aim to reduce firing temperature for ceramic body (from 1250°C to 1170°C). This is achieved substituting feldspar and quartz with recycled blend materials and a little percentage of flux (less than 3%). Further, we introduced in sanitary ware vitreous-china formulation a waste glass, granitic materials and fired broken ceramic pieces. Tests performed on the "Sanitser" formula showed that it has the same final physical–chemical characteristics of the industrial Vitreous China (VC) body. However, different ceramic pieces (wash basin, bidet and WC pan) are compared with VC production. The results allowed us that Sanitser body can replace Vitreous China in the Sanitaryware production. In this project, the firing temperature of the ceramic body is reduced significantly with a supposed decrease of the CO_2 emissions. We utilized, in Sanitser formulation, about 43.62% of recycled materials that would end in dumps.
Keywords: waste glass ceramic, porcelain, slip casting, thermal application.

Resumo

Neste artigo, são apresentados os resultados do projeto europeu LIFE "Sanitser". Este trabalho teve como objetivo reduzir a temperatura de queima da massa cerâmica (de 1250°C para 1170°C). Isto foi obtido substituindo a mistura de feldspato e quartzo por materiais reciclados e uma pequena percentagem de fundente (menos do que 3%). Além disso, foi introduzida na formulação de massa de sanitário vitrificado chinês resíduos de vidro, granito e materiais cerâmicos quebrados após queima. Os testes realizados mostraram que a formulação "Sanitser" apresenta as mesmas propriedades físicas e químicas da cerâmica vitrificada chinesa (VC). No entanto, várias peças de cerâmica (lavatório, bidé e vaso sanitário) foram comparadas com a produção de VC. Os resultados obtidos permitiram afirmar que a massa "Sanitser" pode substituir a massa VC na produção industrial. Neste projeto a temperatura de queima do corpo cerâmico é significativamente reduzida com a suposta redução das emissões de CO_2. Utilizou-se na formulação "Sanitser", cerca de 43,62% de materiais reciclados que acabariam em aterros sanitários.
***Palavras-chave**: vitrocerâmica, porcelana, colagem de barbotina, aplicação térmica*

1. INTRODUCTION

The aim of this research is to replace or in part the "hard" materials (feldspar and quartz), used for vitreous china sanitaryware slip, with recovery and recycled materials. The Vitreous China bodies normally used in the sanitaryware casting [1-5], are in general a mix of clays (20-28%), kaolins (25-35%), quartz (17-31%) and feldspar (15-23%). The feldspar is a mixture of silica-aluminates and/or earth alkaline; the most important for the vitreous china sanitaryware industry are:

- Orthoclase ($KAlOSi_3O_8$) that is the main constituent of potassium feldspar; it has a very long melting range, gives a very viscous glaze and it has an incongruent melting around 1150°C
- Albite ($NaAlSi_3O_8$) that is the main constituent of sodium feldspar; it melts congruently at 1118°C but it has a shorter melting range and gives less viscous glass compared to potassium feldspar.

Feldspars used in the industry are never pure but are a combination of the above mentioned to get the best compromise between viscosity, melting temperature, and melting range. In fact, the feldspar guarantees ending of vitrification process in the Vitreous china pieces fired around 1250°C [1, 2, 6, 7]. Quartz is a material of primary importance; it has an action on the sanitary ware bodies that can be summarised as follows:

- it corrects plasticity; being a non-plastic material, it reduces plasticity;
- it increases the whiteness of the finished product, given that it normally only contains small quantities of iron and/or titanium;
- it makes it possible to vary the body's expansion coefficient;
- it increases the body's vitrification temperature;

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- by its combination, in part, with feldspathic glass, mullite is formed that, together with the residue quartz, makes up the “framework” of the ceramic body that contrasts its deformation during firing [1, 2, 6, 7].

In Sanitser formula we insert a blend of waste glass, granite and fired broken VC pieces, provided by Minerali Industriali srl, for replacement the “hard” raw materials (quartz and feldspar). Different concentrations of this mix are tested and at the end a sanitaryware body slip are produced. In this paper, we present the data obtained on the final formula. Previous researches, on the use of waste glasses in industrial products, have been published proving that such material can be an alternative to traditional constituents [8-12]. In particular, waste glass can replace feldspar, as reported in many papers in literature, in ceramics body [13-17].

Although in literature, [18-20] is obvious that for ceramics, formed by slip casting, the presence of glass produces problems on stabilizing the cast slip, in our study we overcame these problems with proper measures.

In fact, in sanitary ware process the VC body must be respect a series of parameters, in particular:

- Guarantee right rheological properties to permits the casting: Gallenkamp viscosity around 300-330 °G, Thixotropy after 1 minute around 20-30 °G, thickness after 1 hour at least 7 mm.
- Have a flexural resistance above 2 MPa in raw pieces, and above 40 MPa in final products to avoid breakages respectively during the handling and the use.
- Present a final shrinkage less than 12% to preserve original piece design
- Be in dilatometric according with the glaze to avoid defects like crazing and peeling.
- Have final water absorption less than 0.5 % to guarantee hygiene during the product life.

In our formula, we verify all these parameters and compared the values held, with those of standard vitreous china. On the Sanitser, body is carried out the forming process of sanitaryware, in a pilot plant, without changing the phases of the traditional casting [1, 2, 21-23]. Obviously, sanitaryware products must to respect several boundaries to guarantee safety, hygiene and aesthetic properties. Therefore, the sanitary ware pieces, produced in Sanitser project, are tested in compliance to European and Italian norms: in particular, EN 997, EN 14528 and EN 14688 that allow the CE marking, and UNI 4543. The latter describes the test methods adopted for verify chemical and physical resistance of the ceramic mass and glaze [24-27].

2. MATERIALS

2.1. Raw Materials

Hycast Rapide ball clay, Hycast VC ball clays, Flux, Remblend kaolin furnished by Imerys Ceramics srl, Italy; Sanblend 90 Ball Clay, HPC kaolin and CC31 kaolin provided by Sibelco Spa, Italy; Imperial kaolin furnished by Sedlecky Caolin AS, Turkey; BB-Z kaolin, Ceramic Blend (composed of Glass Filler GS-VF, Pitcher BVC-VF, "F60-PBVF") provided by Minerali Industriali srl, Italy.

In table 1 shown the technical data of the recycled materials, insert in the mix, supplied by Minerali industriali srl.

The waste glass “GS-VF” comes from glass bottle, the pitcher “BVC-VF” comes from recovery of sanitary ware ceramics production and "F60-PBVF" is the recovery of the Verbania "historical" white granite quarries.

Table 1. Average chemical composition and granulometric parameter of recycled materials, insert in blend formulation, used in Sanitser body.

Chemical composition	Glass Filler GS-VF	Granite "F60-PBVF"	Pitcher BVC-VF
SiO_2	71.7	77.10	70.80
Al_2O_3	2.70	13.00	22.00
Fe_2O_3	0.42	0.10	0.60
TiO_2	0.07	0.02	0.40
CaO	9.50	1.10	0.70
MgO	2.00	0.08	0.25
K_2O	1.00	4.70	1.40
Na_2O	12.50	3.40	3.60
L.O.I.	0.10	0.30	0.25
Retained on 75 mm sieve	2%	2%	< 3%

2.2. ***Vitreous China formulations***

The casting slip Sanitser is formulated and prepared in laboratory and in pilot plant of the SE.TE.C. srl, using the raw materials, cited above, while the standard vitreous china slip, used for a comparison, came from a sanitary ware factory. In table 2 we reported the composition percentage for both the slips. As shown in table 2 the percentage of the raw materials recycled in Sanitser body is about of 43.62% of the dry weight of the body.

Table 2. Comparison of sanitaryware bodies composition.

Raw materials	Sanitser body composition (%)	Tradition vitreous china composition (%)
Ball clays	24%	24%
Kaolins	30%	29.5%
Ceramic Blend (waste glass 9.5% +granite +pitcher)	43.62%	/
Quartzs	/	27.50%
Feldspars	/	19.00%
Fluxes	2.38%	/

2.3. Equipments for laboratory tests

Universal torsion viscometer, (model TV/30/A, Gallenkamp type), stove thermostat, bending test machine (mod. Mor/1), electronic balances (BE/95 series) supplied by Ceramics Instruments (Sassuolo, Italy); electric gradient kiln, electronic caliper proved by Gabbrielli srl (Calenzano (FI), Italy); gypsum mould and laboratory mixer made in SE.TE.C. srl (Civita Castellana, Italy), electronic dilatometer (mod. DIL 402) by NETZSCH, Gerätebau GmbH (Selb, Germany), Heating Microscope (Misura HSM/ HSML) by TA Instruments (New Castle, Delaware, USA).

2.4. Preparation of Sanitser slurry

SE.TE.C. srl equipments present in pilot plant for produce sanitary ware are: Turboblunger 2nd phase (0.5 m^3), Turboblunger 1st phase (1 m^3), Vibrating sieve 1st and 2nd phase with de-ironing, Tank with slow agitator 1st and 2nd phase, Casting bench, Intermittent dryer, Glazing plant, Kiln (1m^3). Tests are performed with two bodies that are developing in table 2. In Sanitser slurry, the raw materials and water are mixed as in the production cycle, normally used in VC sanitary ware industry. To prepare slips entails the following main phases:

1) Dispensing of raw materials, dissolving of clays, Glass Filler GS-VF and water (1st phase) inside the mixers or turbine mixers of 1st phase;
2) Sieving and deferrization of the fraction obtained;
3) Mixing of the clayey suspension with kaolins, pitcher “BVC-VF”, Talc, granite "F60-PBVF" (2nd phase), again inside the turbine mixers of 2nd phase;
4) Sieving and deferrization of the body obtained;
5) Maturing of slip inside slow propeller-mixers.

The VC body is stored in wells equipped with slow mixers until it needs to be sending via pumps to the central casting tubes to serve single machines or manual casters.

Viscosity, thixotropy of the slip at 1 minute and litre weight are checked on the slip preparations after ageing. To get better dispersion 0.5% sodium silicate is added to the slurry before mixing. In Sanitser body, this deflocculant is not inserting in the first phase.

2.5. Equipments for pre-industrial tests

Sanitary ware manufacturing/production process consists of different steps from body preparation to firing. They are:

- Body preparation (described in section 2.3)
- Glaze preparation
- Moulding/Mould Preparation
- Casting
- Drying
- Control & Spraying
- Firing

3. METHODS

3.1. Sanitser characterization in laboratory

The characterizations of the slips are made according to the method adopted in the sanitary ware industry. The prepared Sanitser body is casted into plaster mould at room temperature, holding a series of samples necessary for perform some physical parameters of the dry and fired slip:

1. Rheological test: we made a liquid slip to measure its viscosity and thixotropy after 1 minute by a Gallenkamp viscometer.
2. Thickness formation and consolidation test: the slip is casted in a gypsum cup, a drain type mould, in which the excess of the slip is drain away after 1 hour. After about 30 minutes, thickness of the body formed on the cup’s wall and humidity of the piece are measured.

3. Modulus of rupture (MOR) i.e. 3 point flexural testing: 10 rectangular bars are prepared, casting slip in plaster mould with dimensions 150mmx30mmx20mm. After 1.5 hour, excess of slip is poured away from the mould. The samples are removed from the mould and allowed to dry at 40°C for 1 day by stove. The resistances to bending of the specimens are measured by a bending test machine.
4. Linear fired shrinkage percentage: 3 rectangular bars are prepared casting the slip in plaster mould with dimensions 200mmx30mmx20mm. After 2.0 hours the excess of slip is poured away from the mould, and samples are allowed to dry in stove at 40°C for 1 day. The green specimens are fired at 1165-1170°C in a laboratory gradient kiln. Following ASTM (designation C326-82) [28] and UNI 4543 [27], the linear shrinkage is calculated by the equation: LS% = (Ls-Lc/Ls) x 100; being Ls and Lc the length (mm) of the green and fired specimens respectively.
5. Water absorption percentage: It is determined via boiling in distilled water for 2 hours and by immersing in water for 1 day. Then the specimens are removed from water, dried with a cotton cloth then weighed. It is calculated following ASTM (designation C373-88) [29], EN 997 [24] and UNI 4543 [27] norms. In these methods, samples are exposed to saturation of water. Saturation can be achieved through boiling or vacuum, depending on the method.

At this point, it is necessary, before switching to the pre-industrial stage of sanitary ware casting, to analyse the behaviour of the body in firing process and its dilatometric agreement with glaze. A dilatometric analysis on fired pieces is performed, while on the dry slip is carried out a vitrification curve by heating microscope. The slips powder sintering in air is followed by optical heating microscope (Expert System Solutions, Misura ODHT-HSM, Modena, Italy) at 10°C/min in the temperature range of about 900 –1300°C. At the end, a quantitative X-Ray Diffraction (XRD) is carried out. This is a typical technique for routine quality control of powders and materials discovery. Quantitative XRD (D5000, Siemens AG, Erlangen, Germany) and full structure refinement can be used to characterise SANITSER body slip at different temperature in order to verify the phase composition.

3.2. Pre-industrial tests :Body preparation and casting process

At this stage in the pilot plant of the SETEC's staff proceeds to the body preparation and after to the casting of a series of articles, basins and WC pans. The casting process permit to identify how the Sanitser body slip behaves with different shapes and different geometries. Further, we can see deformations and defects that may be encountered on the specific pieces. The pieces production, in SETEC pilot plant, are organized as described in paragraph 2.4, in which is assembly the plaster moulds of different wash basin models and WC pans in automatic benches for casting.

4. RESULTS AND DISCUSSIONS

On Sanitser body slip are carried out a series of tests with the aim to compare its physical - chemical characteristics with vitreous china used in industrial plants. In particular have been performed:

- **Rheological test:** This test allows to simulate the production conditions and so to evaluate body castability and its deflocculants request of the body. As reported in table 3 Sanitser body slip not needed deflocculant as sodium silicate. It is due to the introduction of recycled glass material. As reported in literature [18-20] the waste glass introduction in ceramic formulation has an alkalinizing effect (change pH). Using waste glass, we expected the release of the sodium and calcium ions to form their respective hydroxides [18-20]. Indeed this latter release gives to a deflocculant action, in fact this cause the viscosity and thixotropy decrease. The deflocculating effect of glass is similar to sodium silicate. We change the body preparation procedure, adding the glass directly in the first phase without sodium silicate, therefore. Only a little percentage of polyacrylate deflocculant (about 0.08% w/w) is used in 2nd phase. Further, thickness formation after 60 minutes is the same than vitreous china and this confirms Sanitser castability.
- **Flexural test**: this test allows an evaluation of mechanical properties both in raw than in fired pieces. Raw flexural resistance is important during industrial production because it allows to avoid abrupt brakeage because of handling and fissuring during the drying time caused by moisture gradients. For these reasons, high raw mechanical resistance means to reduce scraps and so to improve the productivity [30, 31]. Instead fired flexural resistance, in according to normative EN 14688, EN 14528 and EN 997, it is important because it guarantees safety condition during the product life cycle. Indeed an abrupt piece breakage could be very dangerous. As reported in table 3, results are very good both in raw than in fired sample. For these reason Sanitser formulation is in according to the normative [24-26].
- **Linear shrinkage**: it lets to evaluate the sintering behaviour of the fired samples and the final product dimension [28, 32]. Normally in the VC pieces is accepted final shrinkage lower than 12 %. Indeed bigger values would mean unacceptable deformation.
- **Water absorption**: Low values of water adsorption or porosity suggest a high degree of vitrification [29, 33]. Instead, low water absorption (< 0.5 %) is fundamental to guarantees hygiene during the product life cycle, in

particular for WC pans. So we made test in according to normative EN 997 and UNI 4543 [24, 27]. As reported in table 3 also in these case Sanitser formula is very similar to a vitreous china body.

The parameters, obtained for Sanitser are compared with those one industrial slip, as described in paragraph 3.1, and are shown in table 3.

Table 3. Characteristic data obtained from Sanitser slip compared with industrial vitreous china slip. (Each value is the mean of five determinations).

Technical parameters	Industrial slip fired at 1250°C RSD% ≤ 5.0	Sanitser slip fired at 1165°C RSD% ≤ 5.0
Density (g/cm^3)	1.800	1800
Moisture (%)	32-35	34.3
Viscosity (°G)	305	295
Sodium silicate deflocculant (%)	0.17	/
Sodium carbonate deflocculant (%)	0.07	0.07
Polyacrylate deflocculant (%)	/	0.05
Thixotropy (after 1 minute) (°G)	25-35	30
Deformation (mm)	40-43	43
Thickness after 1 h (mm)	6.5-7.0	6.6
Modulus of rupture (MOR) (kg/cm^2)	24-25	25.3
Resistance to bending after firing (MPa) (UNI 4543 required a value > 39.50 MPa)	49.5	55.7
Linear fired Shrinkage (%)	12-13	12.6
Water absorption (%) (EN 997 and UNI 4543 required a value < 0.5%)	< 0.5	0.1

In Sanitser slip, rheological parameters (as viscosity, thixotropy and density), have characteristic values, in line with the range found in VC body, adding water or deflocculants. So, also deformation, thickness, linear shrinkage, water absorption and MOR values fall within the ranges reported for VC body. As regard mechanical properties, the average bending strength of samples VC fired in the 1230-1250ºC range is >39.5±2 MPa, prescribed in the standard UNI 4543 for these ceramic materials. Meanwhile for Sanitser body fired at 1165°C this value increase of about 12%. Sanitser body also showed better mechanical characteristics, attributed to enhanced microstructural homogeneity, as reported in literature for porcelain in which is added waste glass [34, 14].

4.1. Vitrification curve

The best vitrification range is achieved when open porosity reaches a minimum value, be nearly zero, and simultaneously linear shrinkage is maximum. Firing above vitrification range results in a drastic fall of the physical properties due to forced expulsion of the entrapped gases, resulting in blisters and bloating [33, 35]. Figure 1 shown vitrification curve, in which we report the linear shrinkage % and the water absorption % in function of different firing temperature for Sanitser body. This test allow to prove that in SANITSER body the optimum firing temperature is in the 1160º-1180ºC range.

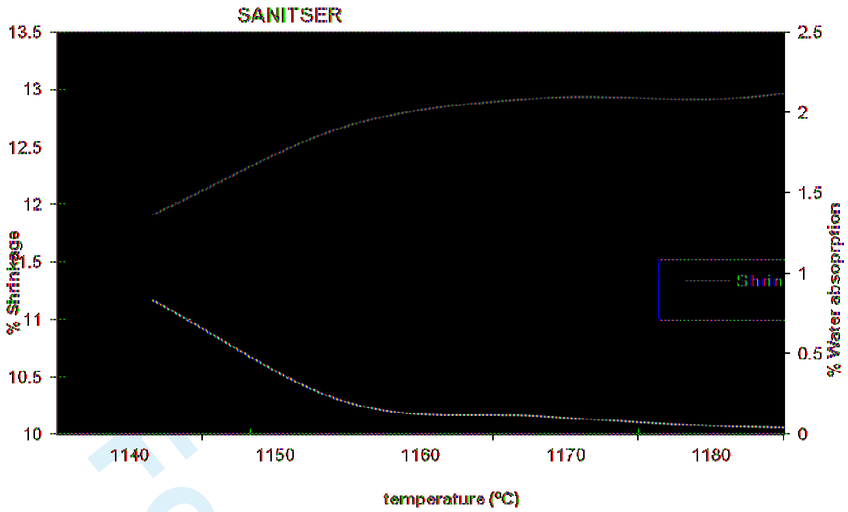

Figure 1. Linear shrinkage and water absorption in function of firing temperature for Sanitser sample.

It's clear from figures that linear shrinkage increases as sintering temperature increase, it is lower in samples sintered at 1170˚C. In vitreous ceramic body, the best range of linear shrinkage is about 12-13% and in this range was satisfied for SANITSER slip fired at 1145-1175°C. During sintering process, porosity ceramic body is reduced. So, shrinkage size is equal to size of pore removed or lost. Sintering temperature has an extreme effect on the value of linear shrinkage as increasing sintering temperature leads to increases linear shrinkage due to increasing amount of molten filling pores and product high shrinkage in the sample. Continuing to increase sintering temperature to 1180˚K, sintering continues more and more resulting lower porosity and from here higher shrinkage.

4.2. Dilatometric behaviour

It is also used to check the progress of chemical reactions, particularly those displaying a large molar volume change, as the rate of phase changes [1, 2, 36, 37]. Another common application of a dilatometer is the measurement of thermal expansion. The dilatometer allows recording materials' expansions and contractions by using a contact method [1, 2, 36, 37] in compliance with ASTM E228-11 [38]. In table 4 are reported coefficients expansion "α" for both the slips. As shown in table 4 Sanitser formulation has values compatibles with sanitaryware bodies' standard.

Table 4. Comparison of dilatometric coefficients obtained from Sanitser slip compared with industrial standard vitreous china slip.

Temperature range (°C)	Dilatometric coefficient α in Vitreous china standard (1/K)	Dilatometric coefficient α in SANITSER body (1/K)
50-200	65.6 x10^{-7}	67.8 x10^{-7}
50-300	64.5 x10^{-7}	68.9 x10^{-7}
50-400	65.5 x10^{-7}	69.8 x10^{-7}
50-500	66.7 x10^{-7}	70.7 x10^{-7}
50-650	71.2 x10^{-7}	74.1 x10^{-7}
300-500	69.5 x10^{-7}	72.9 x10^{-7}
500-650	84.6 x10^{-7}	84.3 x10^{-7}

4.3. Heating microscope

This analysis permits us to photograph firing body behavior [39-42]. As shown in figure 2, Sanitser formulation presents a firing curve shifted towards lower temperatures, with a greater slope between 1110 °C and 1250°C. After 1250 °C the Sanitser slip shows a trend entirely different from that of the body of VC standard. This behaviour due to the glass effects in the mullite formation [43] and over 1250°C it is possible to see an expansion of the sample certainly due to forming gases. This analysis lets to confirm that Sanitser formulation has a low firing behaviour.

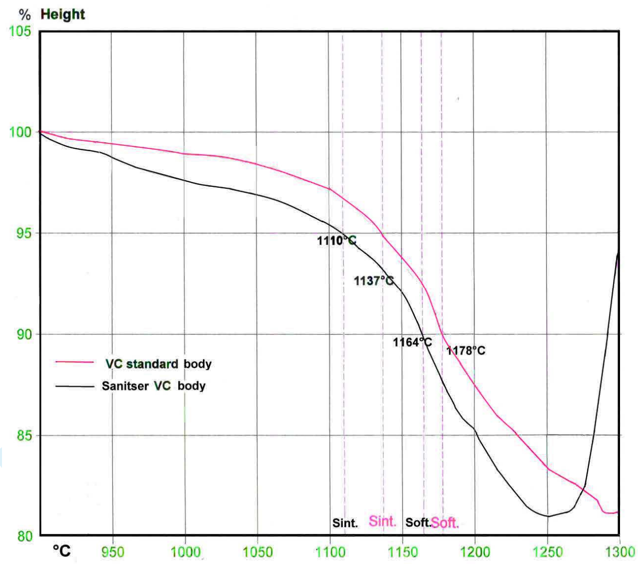

Figure 2. Firing behaviour for Sanitser body compared with standard VC by heating microscope.

4.4. XRPD ((X-ray powder diffraction) analysis

The formation of mullite is conducted, at lower temperatures, to precisely effect the waste glass [43-46]. Therefore, we have verified forming crystallographic phases in Sanitser body through XRPD analysis. This has allowed us to confirm the formation of mullite by the Rietveld method [43-46]. Mullites is synthesized by firing the starting material (Sanitser body) at various temperatures. With this method, it is possible to control quantitatively the amount of crystalline phases and of the remaining amorphous phase. The major phase present after firing is the vitreous phase (from 58% to 63%). The major crystalline phases are quartz (14-18%) and mullite (11-18%). Minor amounts of feldspar (plagioclase) and cristobalite also are present (see figure 3).

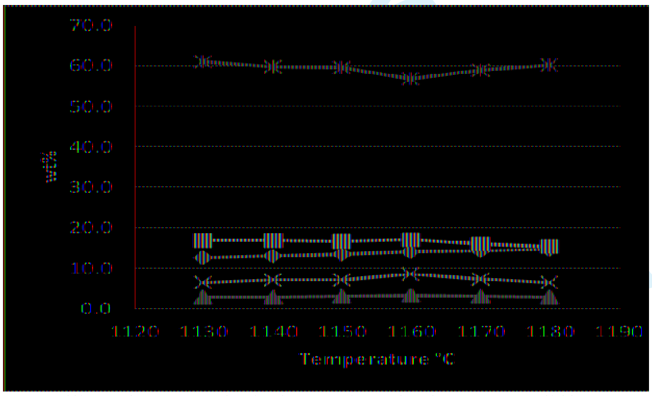

Figure 3. Crystalline phases analysis for Sanitser body (VC) at different temperature

The Sanitser body has a comparable ratio between crystalline phases and amorphous phase, at lower temperatures of about 80°C, than the traditional vitreous china. This ratio, between amorphous and crystalline component, remains almost constant in the entire temperature range explored. This suggests us that transformations occur in the body takes place at temperatures slightly higher to 1110 °C. A detailed analysis of phases shows, in fact, that their contents unchanged from 1120 to 1180°C, except for an increase of mullite and a decrease of other crystalline phases at high temperatures (above 1200 °C).

Pre-industrial test: This is the most important test because it reproduces production conditions and lets to do a comparison between Sanitser formulation and Vitreous China. To realize these trials we casted, glazed and fired about 60 real pieces (wash basin, WC pans and bidet) maintaining same working time and rheological condition used in factory. All casted pieces are sprayed using a low firing glaze, developed specifically for this project, and fired at

1170°C. The kiln present in our pilot plant kilns, according to the type of heating system adopted, is gaseous shuttle kiln. In the kiln is set to a firing curve, shown in figure 4. The firing curve used for the Sanitser slip is of about 17 h, in comparison to that of an industrial cycle that has duration of about 19-22 hours.

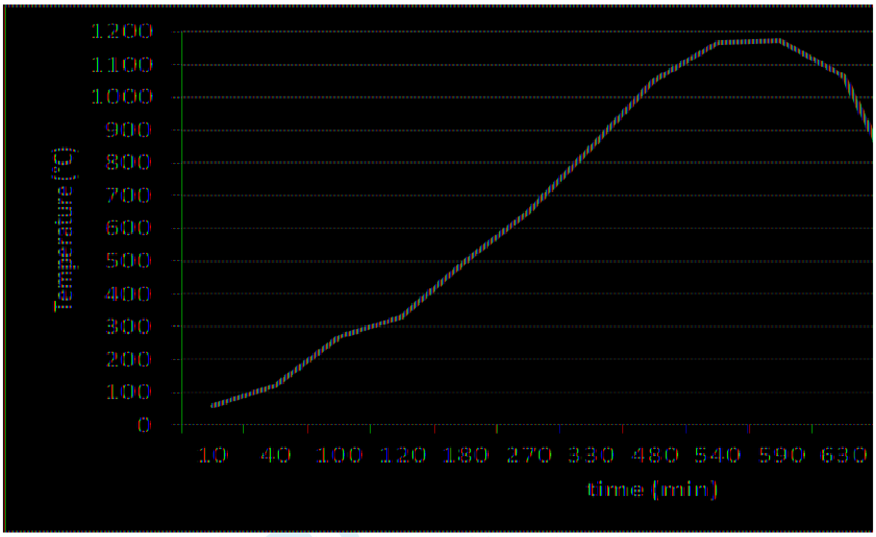

Figure 4. Firing curve used for Sanitser pieces.

The lower firing temperature and a shorter firing cycle confirm that if Sanitser slip is used in industry it would be getting an important decrease of CO_2 and of energy necessary for firing the sanitary ware.

In figure 5 are shown several sanitaryware products obtained in Sanitser project. In pre-industrial production, we did not observe any differences respect to a Vitreous China pieces. Indeed Sanitser raw and fired scraps are comparable to Vitreous china case. Furthermore, it's important to underline that we realized different shapes to demonstrate Sanitser castability.

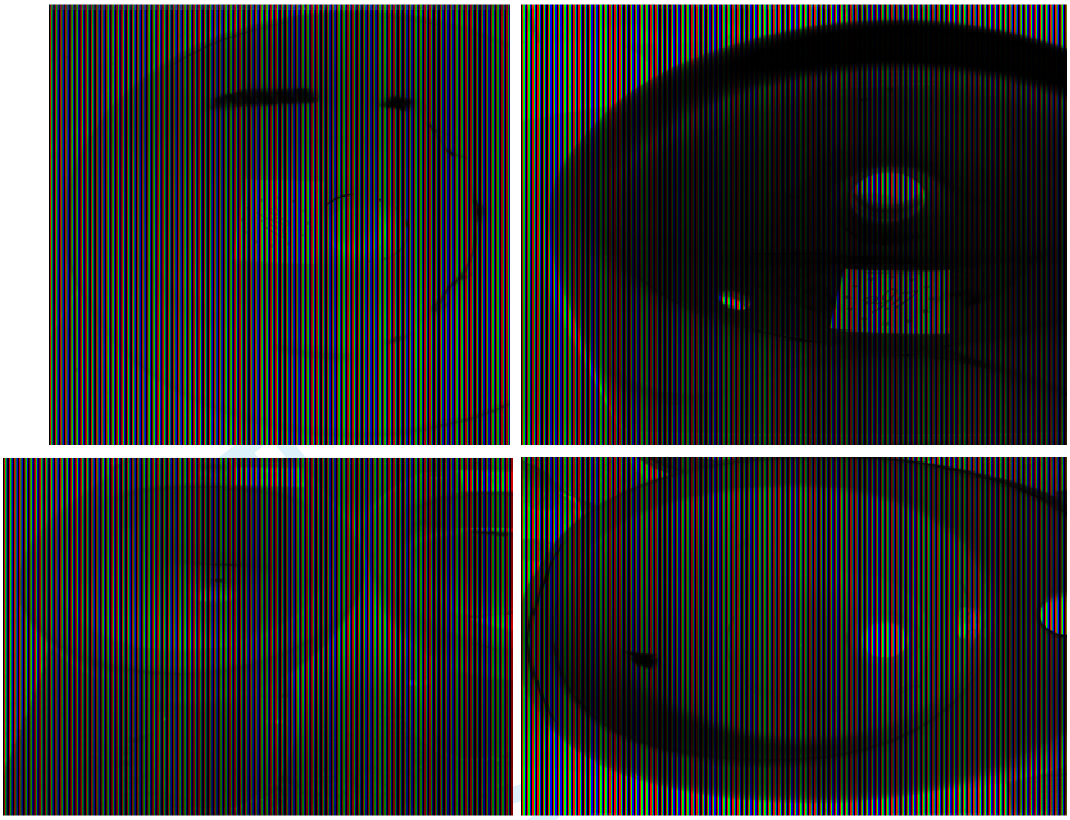

Figure 5. Wash basins, WC pan and bidets produced with Sanitser body.

5. CONCLUSIONS

In this paper, we summarized Sanitser Life project results and we proved that is possible to low vitreous China bodies firing temperature from 1250°C to 1170°C. To get this aim we substituted the feldspar and quartz introducing a blend (supplied by Minerali Industriali srl) in a final percentage of about 43.62% w/w of the total formula.

To confirm these conclusions we make several trials, which allowed us to compare Sanitser formulation with standard VC body. All tests confirm that is possible to low firing temperature without jeopardizing properties normally wanted in sanitaryware. Indeed there are not differences about rheological and mechanical properties, shrinkage and water absorption. Sanitser slip and the pieces held with it overcome EN norms and satisfy industrial parameters. Besides preindustrial trials confirm good results obtained and the next steps involve the industrialization of the Sanitser slip. The novelty of this research isn't the waste glass insertion in ceramic formulas, as today it is used especially in the tile industry, but for the first time we overcome the rheological problems despite the higher percentage of waste glass, amounted to 9.5%.

Also for the first time in a VC body, we have replaced the hard raw materials (quartz and feldspar) with recycled materials with low contents of free silica. This allows to obtain a ceramic body less dangerous to the workers health. Finally a technological level the possibility to bake the VC body at a lower temperature of about 80 ° C, can allow an energy saving and a consequent reduction in CO_2 emissions.

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"SANITSER", AN INNOVATIVE SANITARYWARE BODY, FORMULATED WITH WASTE GLASS AND RECYCLED MATERIALS.

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Abstract

In the present paper we present the results of "Sanitser" Life European project. In this latter we worked with the aim to reduce firing temperature for ceramic body (from 1250°C to 1170°C). This is achieved substituting feldspar and quartz with recycled blend materials and a little percentage of flux (less than 3%). Further, we introduced in sanitary ware vitreous-china formulation a waste glass, granitic materials and fired broken ceramic pieces. Tests performed on the "Sanitser" formula showed that it has the same final physical–chemical characteristics of the industrial Vitreous China (VC) body. However, different ceramic pieces (wash basin, bidet and WC pan) are compared with VC production. The results allowed us that Sanitser body can replace Vitreous China in the Sanitaryware production. In this project, the firing temperature of the ceramic body is reduced significantly with a supposed decrease of the CO_2 emissions. We utilized, in Sanitser formulation, about 43.62% of recycled materials that would end in dumps.
Keywords: waste glass ceramic, porcelain, slip casting, thermal application.

Resumo

Neste artigo, são apresentados os resultados do projeto europeu LIFE "Sanitser". Este trabalho teve como objetivo reduzir a temperatura de queima da massa cerâmica (de 1250°C para 1170°C). Isto foi obtido substituindo a mistura de feldspato e quartzo por materiais reciclados e uma pequena percentagem de fundente (menos do que 3%). Além disso, foi introduzida na formulação de massa de sanitário vitrificado chinês resíduos de vidro, granito e materiais cerâmicos quebrados após queima. Os testes realizados mostraram que a formulação "Sanitser" apresenta as mesmas propriedades físicas e químicas da cerâmica vitrificada chinesa (VC). No entanto, várias peças de cerâmica (lavatório, bidé e vaso sanitário) foram comparadas com a produção de VC. Os resultados obtidos permitiram afirmar que a massa "Sanitser" pode substituir a massa VC na produção industrial. Neste projeto a temperatura de queima do corpo cerâmico é significativamente reduzida com a suposta redução das emissões de CO_2. Utilizou-se na formulação "Sanitser", cerca de 43,62% de materiais reciclados que acabariam em aterros sanitários.
Palavras-chave*: vitrocerâmica, porcelana, colagem de barbotina, aplicação térmica*

1. INTRODUCTION

The aim of this research is to replace or in part the "hard" materials (feldspar and quartz), used for vitreous china sanitaryware slip, with recovery and recycled materials. The Vitreous China bodies normally used in the sanitaryware casting [1-5], are in general a mix of clays (20-28%), kaolins (25-35%), quartz (17-31%) and feldspar (15-23%). The feldspar is a mixture of silica-aluminates and/or earth alkaline; the most important for the vitreous china sanitaryware industry are:

- Orthoclase ($KAlOSi_3O_8$) that is the main constituent of potassium feldspar; it has a very long melting range, gives a very viscous glaze and it has an incongruent melting around 1150°C
- Albite ($NaAlSi_3O_8$) that is the main constituent of sodium feldspar; it melts congruently at 1118°C but it has a shorter melting range and gives less viscous glass compared to potassium feldspar.

Feldspars used in the industry are never pure but are a combination of the above mentioned to get the best compromise between viscosity, melting temperature, and melting range. In fact, the feldspar guarantees ending of vitrification process in the Vitreous china pieces fired around 1250°C [1, 2, 6, 7]. Quartz is a material of primary importance; it has an action on the sanitary ware bodies that can be summarised as follows:

- it corrects plasticity; being a non-plastic material, it reduces plasticity;
- it increases the whiteness of the finished product, given that it normally only contains small quantities of iron and/or titanium;
- it makes it possible to vary the body's expansion coefficient;
- it increases the body's vitrification temperature;

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- by its combination, in part, with feldspathic glass, mullite is formed that, together with the residue quartz, makes up the "framework" of the ceramic body that contrasts its deformation during firing [1, 2, 6, 7].

In Sanitser formula we insert a blend of waste glass, granite and fired broken VC pieces, provided by Minerali Industriali srl, for replacement the "hard" raw materials (quartz and feldspar). Different concentrations of this mix are tested and at the end a sanitaryware body slip are produced. In this paper, we present the data obtained on the final formula. Previous researches, on the use of waste glasses in industrial products, have been published proving that such material can be an alternative to traditional constituents [8-12]. In particular, waste glass can replace feldspar, as reported in many papers in literature, in ceramics body [13-17].

Although in literature, [18-20] is obvious that for ceramics, formed by slip casting, the presence of glass produces problems on stabilizing the cast slip, in our study we overcame these problems with proper measures.

In fact, in sanitary ware process the VC body must be respect a series of parameters, in particular:

- Guarantee right rheological properties to permits the casting: Gallenkamp viscosity around 300-330 °G, Thixotropy after 1 minute around 20-30 °G, thickness after 1 hour at least 7 mm.
- Have a flexural resistance above 2 MPa in raw pieces, and above 40 MPa in final products to avoid breakages respectively during the handling and the use.
- Present a final shrinkage less than 12% to preserve original piece design
- Be in dilatometric according with the glaze to avoid defects like crazing and peeling.
- Have final water absorption less than 0.5 % to guarantee hygiene during the product life.

In our formula, we verify all these parameters and compared the values held, with those of standard vitreous china. On the Sanitser, body is carried out the forming process of sanitaryware, in a pilot plant, without changing the phases of the traditional casting [1, 2, 21-23]. Obviously, sanitaryware products must to respect several boundaries to guarantee safety, hygiene and aesthetic properties. Therefore, the sanitary ware pieces, produced in Sanitser project, are tested in compliance to European and Italian norms: in particular, EN 997, EN 14528 and EN 14688 that allow the CE marking, and UNI 4543. The latter describes the test methods adopted for verify chemical and physical resistance of the ceramic mass and glaze [24-27].

2. MATERIALS

2.1. Raw Materials

Hycast Rapide ball clay, Hycast VC ball clays, Flux, Remblend kaolin furnished by Imerys Ceramics srl, Italy; Sanblend 90 Ball Clay, HPC kaolin and CC31 kaolin provided by Sibelco Spa, Italy; Imperial kaolin furnished by Sedlecky Caolin AS, Turkey; BB-Z kaolin, Ceramic Blend (composed of Glass Filler GS-VF, Pitcher BVC-VF, "F60-PBVF") provided by Minerali Industriali srl, Italy.

In table 1 shown the technical data of the recycled materials, insert in the mix, supplied by Minerali industriali srl.

The waste glass "GS-VF" comes from glass bottle, the pitcher "BVC-VF" comes from recovery of sanitary ware ceramics production and "F60-PBVF" is the recovery of the Verbania "historical" white granite quarries.

Table 1. Average chemical composition and granulometric parameter of recycled materials, insert in blend formulation, used in Sanitser body.

Chemical composition	Glass Filler GS-VF	Granite "F60-PBVF"	Pitcher BVC-VF
SiO_2	71.7	77.10	70.80
Al_2O_3	2.70	13.00	22.00
Fe_2O_3	0.42	0.10	0.60
TiO_2	0.07	0.02	0.40
CaO	9.50	1.10	0.70
MgO	2.00	0.08	0.25
K_2O	1.00	4.70	1.40
Na_2O	12.50	3.40	3.60
L.O.I.	0.10	0.30	0.25
Retained on 75 mm sieve	2%	2%	< 3%

2.2. *Vitreous China formulations*

The casting slip Sanitser is formulated and prepared in laboratory and in pilot plant of the SE.TE.C. srl, using the raw materials, cited above, while the standard vitreous china slip, used for a comparison, came from a sanitary ware factory. In table 2 we reported the composition percentage for both the slips. As shown in table 2 the percentage of the raw materials recycled in Sanitser body is about of 43.62% of the dry weight of the body.

Table 2. Comparison of sanitaryware bodies composition.

Raw materials	Sanitser body composition (%)	Tradition vitreous china composition (%)
Ball clays	24%	24%
Kaolins	30%	29.5%
Ceramic Blend (waste glass 9.5% +granite +pitcher)	43.62%	/
Quartzs	/	27.50%
Feldspars	/	19.00%
Fluxes	2.38%	/

2.3. Equipments for laboratory tests

Universal torsion viscometer, (model TV/30/A, Gallenkamp type), stove thermostat, bending test machine (mod. Mor/1), electronic balances (BE/95 series) supplied by Ceramics Instruments (Sassuolo, Italy); electric gradient kiln, electronic caliper proved by Gabbrielli srl (Calenzano (FI), Italy); gypsum mould and laboratory mixer made in SE.TE.C. srl (Civita Castellana, Italy), electronic dilatometer (mod. DIL 402) by NETZSCH, Gerätebau GmbH (Selb, Germany), Heating Microscope (Misura HSM/ HSML) by TA Instruments (New Castle, Delaware, USA).

2.4. Preparation of Sanitser slurry

SE.TE.C. srl equipments present in pilot plant for produce sanitary ware are: Turboblunger 2nd phase (0.5 m^3), Turboblunger 1st phase (1 m^3), Vibrating sieve 1st and 2nd phase with de-ironing, Tank with slow agitator 1st and 2nd phase, Casting bench, Intermittent dryer, Glazing plant, Kiln (1m^3). Tests are performed with two bodies that are developing in table 2. In Sanitser slurry, the raw materials and water are mixed as in the production cycle, normally used in VC sanitary ware industry. To prepare slips entails the following main phases:

1) Dispensing of raw materials, dissolving of clays, Glass Filler GS-VF and water (1st phase) inside the mixers or turbine mixers of 1st phase;
2) Sieving and deferrization of the fraction obtained;
3) Mixing of the clayey suspension with kaolins, pitcher “BVC-VF”, Talc, granite "F60-PBVF" (2nd phase), again inside the turbine mixers of 2nd phase;
4) Sieving and deferrization of the body obtained;
5) Maturing of slip inside slow propeller-mixers.

The VC body is stored in wells equipped with slow mixers until it needs to be sending via pumps to the central casting tubes to serve single machines or manual casters.

Viscosity, thixotropy of the slip at 1 minute and litre weight are checked on the slip preparations after ageing. To get better dispersion 0.5% sodium silicate is added to the slurry before mixing. In Sanitser body, this deflocculant is not inserting in the first phase.

2.5. Equipments for pre-industrial tests

Sanitary ware manufacturing/production process consists of different steps from body preparation to firing. They are:

- Body preparation (described in section 2.3)
- Glaze preparation
- Moulding/Mould Preparation
- Casting
- Drying
- Control & Spraying
- Firing

3. METHODS

3.1. Sanitser characterization in laboratory

The characterizations of the slips are made according to the method adopted in the sanitary ware industry. The prepared Sanitser body is casted into plaster mould at room temperature, holding a series of samples necessary for perform some physical parameters of the dry and fired slip:

1. Rheological test: we made a liquid slip to measure its viscosity and thixotropy after 1 minute by a Gallenkamp viscometer.
2. Thickness formation and consolidation test: the slip is casted in a gypsum cup, a drain type mould, in which the excess of the slip is drain away after 1 hour. After about 30 minutes, thickness of the body formed on the cup’s wall and humidity of the piece are measured.

3. Modulus of rupture (MOR) i.e. 3 point flexural testing: 10 rectangular bars are prepared, casting slip in plaster mould with dimensions 150mmx30mmx20mm. After 1.5 hour, excess of slip is poured away from the mould. The samples are removed from the mould and allowed to dry at 40°C for 1 day by stove. The resistances to bending of the specimens are measured by a bending test machine.
4. Linear fired shrinkage percentage: 3 rectangular bars are prepared casting the slip in plaster mould with dimensions 200mmx30mmx20mm. After 2.0 hours the excess of slip is poured away from the mould, and samples are allowed to dry in stove at 40°C for 1 day. The green specimens are fired at 1165-1170°C in a laboratory gradient kiln. Following ASTM (designation C326-82) [28] and UNI 4543 [27], the linear shrinkage is calculated by the equation: LS% = (Ls-Lc/Ls) x 100; being Ls and Lc the length (mm) of the green and fired specimens respectively.
5. Water absorption percentage: It is determined via boiling in distilled water for 2 hours and by immersing in water for 1 day. Then the specimens are removed from water, dried with a cotton cloth then weighed. It is calculated following ASTM (designation C373-88) [29], EN 997 [24] and UNI 4543 [27] norms. In these methods, samples are exposed to saturation of water. Saturation can be achieved through boiling or vacuum, depending on the method.

At this point, it is necessary, before switching to the pre-industrial stage of sanitary ware casting, to analyse the behaviour of the body in firing process and its dilatometric agreement with glaze. A dilatometric analysis on fired pieces is performed, while on the dry slip is carried out a vitrification curve by heating microscope. The slips powder sintering in air is followed by optical heating microscope (Expert System Solutions, Misura ODHT-HSM, Modena, Italy) at 10°C/min in the temperature range of about 900 –1300°C. At the end, a quantitative X-Ray Diffraction (XRD) is carried out. This is a typical technique for routine quality control of powders and materials discovery. Quantitative XRD (D5000, Siemens AG, Erlangen, Germany) and full structure refinement can be used to characterise SANITSER body slip at different temperature in order to verify the phase composition.

3.2. Pre-industrial tests :Body preparation and casting process

At this stage in the pilot plant of the SETEC's staff proceeds to the body preparation and after to the casting of a series of articles, basins and WC pans. The casting process permit to identify how the Sanitser body slip behaves with different shapes and different geometries. Further, we can see deformations and defects that may be encountered on the specific pieces. The pieces production, in SETEC pilot plant, are organized as described in paragraph 2.4, in which is assembly the plaster moulds of different wash basin models and WC pans in automatic benches for casting.

4. RESULTS AND DISCUSSIONS

On Sanitser body slip are carried out a series of tests with the aim to compare its physical - chemical characteristics with vitreous china used in industrial plants. In particular have been performed:

- **Rheological test:** This test allows to simulate the production conditions and so to evaluate body castability and its deflocculants request of the body. As reported in table 3 Sanitser body slip not needed deflocculant as sodium silicate. It is due to the introduction of recycled glass material. As reported in literature [18-20] the waste glass introduction in ceramic formulation has an alkalinizing effect (change pH). Using waste glass, we expected the release of the sodium and calcium ions to form their respective hydroxides [18-20]. Indeed this latter release gives to a deflocculant action, in fact this cause the viscosity and thixotropy decrease. The deflocculating effect of glass is similar to sodium silicate. We change the body preparation procedure, adding the glass directly in the first phase without sodium silicate, therefore. Only a little percentage of polyacrylate deflocculant (about 0.08% w/w) is used in 2nd phase. Further, thickness formation after 60 minutes is the same than vitreous china and this confirms Sanitser castability.
- **Flexural test**: this test allows an evaluation of mechanical properties both in raw than in fired pieces. Raw flexural resistance is important during industrial production because it allows to avoid abrupt brakeage because of handling and fissuring during the drying time caused by moisture gradients. For these reasons, high raw mechanical resistance means to reduce scraps and so to improve the productivity [30, 31]. Instead fired flexural resistance, in according to normative EN 14688, EN 14528 and EN 997, it is important because it guarantees safety condition during the product life cycle. Indeed an abrupt piece breakage could be very dangerous. As reported in table 3, results are very good both in raw than in fired sample. For these reason Sanitser formulation is in according to the normative [24-26].
- **Linear shrinkage**: it lets to evaluate the sintering behaviour of the fired samples and the final product dimension [28, 32]. Normally in the VC pieces is accepted final shrinkage lower than 12 %. Indeed bigger values would mean unacceptable deformation.
- **Water absorption**: Low values of water adsorption or porosity suggest a high degree of vitrification [29, 33]. Instead, low water absorption (< 0.5 %) is fundamental to guarantees hygiene during the product life cycle, in

particular for WC pans. So we made test in according to normative EN 997 and UNI 4543 [24, 27]. As reported in table 3 also in these case Sanitser formula is very similar to a vitreous china body.

The parameters, obtained for Sanitser are compared with those one industrial slip, as described in paragraph 3.1, and are shown in table 3.

Table 3. Characteristic data obtained from Sanitser slip compared with industrial vitreous china slip. (Each value is the mean of five determinations).

Technical parameters	Industrial slip fired at 1250°C RSD% ≤ 5.0	Sanitser slip fired at 1165°C RSD% ≤ 5.0
Density (g/cm^3)	1.800	1800
Moisture (%)	32-35	34.3
Viscosity (°G)	305	295
Sodium silicate deflocculant (%)	0.17	/
Sodium carbonate deflocculant (%)	0.07	0.07
Polyacrylate deflocculant (%)	/	0.05
Thixotropy (after 1 minute) (°G)	25-35	30
Deformation (mm)	40-43	43
Thickness after 1 h (mm)	6.5-7.0	6.6
Modulus of rupture (MOR) (kg/cm^2)	24-25	25.3
Resistance to bending after firing (MPa) (UNI 4543 required a value > 39.50 MPa)	49.5	55.7
Linear fired Shrinkage (%)	12-13	12.6
Water absorption (%) (EN 997 and UNI 4543 required a value < 0.5%)	< 0.5	0.1

In Sanitser slip, rheological parameters (as viscosity, thixotropy and density), have characteristic values, in line with the range found in VC body, adding water or deflocculants. So, also deformation, thickness, linear shrinkage, water absorption and MOR values fall within the ranges reported for VC body. As regard mechanical properties, the average bending strength of samples VC fired in the 1230-1250ºC range is >39.5±2 MPa, prescribed in the standard UNI 4543 for these ceramic materials. Meanwhile for Sanitser body fired at 1165°C this value increase of about 12%. Sanitser body also showed better mechanical characteristics, attributed to enhanced microstructural homogeneity, as reported in literature for porcelain in which is added waste glass [34, 14].

4.1. Vitrification curve

The best vitrification range is achieved when open porosity reaches a minimum value, be nearly zero, and simultaneously linear shrinkage is maximum. Firing above vitrification range results in a drastic fall of the physical properties due to forced expulsion of the entrapped gases, resulting in blisters and bloating [33, 35]. Figure 1 shown vitrification curve, in which we report the linear shrinkage % and the water absorption % in function of different firing temperature for Sanitser body. This test allow to prove that in SANITSER body the optimum firing temperature is in the 1160º-1180ºC range.

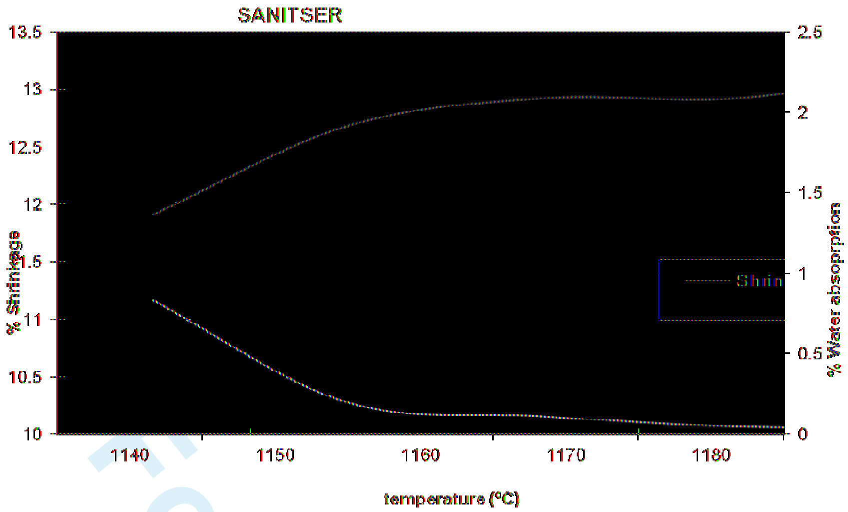

Figure 1. Linear shrinkage and water absorption in function of firing temperature for Sanitser sample.

It's clear from figures that linear shrinkage increases as sintering temperature increase, it is lower in samples sintered at 1170˚C. In vitreous ceramic body, the best range of linear shrinkage is about 12-13% and in this range was satisfied for SANITSER slip fired at 1145-1175°C. During sintering process, porosity ceramic body is reduced. So, shrinkage size is equal to size of pore removed or lost. Sintering temperature has an extreme effect on the value of linear shrinkage as increasing sintering temperature leads to increases linear shrinkage due to increasing amount of molten filling pores and product high shrinkage in the sample. Continuing to increase sintering temperature to 1180˚K, sintering continues more and more resulting lower porosity and from here higher shrinkage.

4.2. Dilatometric behaviour

It is also used to check the progress of chemical reactions, particularly those displaying a large molar volume change, as the rate of phase changes [1, 2, 36, 37]. Another common application of a dilatometer is the measurement of thermal expansion. The dilatometer allows recording materials' expansions and contractions by using a contact method [1, 2, 36, 37] in compliance with ASTM E228-11 [38]. In table 4 are reported coefficients expansion "α" for both the slips. As shown in table 4 Sanitser formulation has values compatibles with sanitaryware bodies' standard.

Table 4. Comparison of dilatometric coefficients obtained from Sanitser slip compared with industrial standard vitreous china slip.

Temperature range (°C)	Dilatometric coefficient α in Vitreous china standard (1/K)	Dilatometric coefficient α in SANITSER body (1/K)
50-200	65.6×10^{-7}	67.8×10^{-7}
50-300	64.5×10^{-7}	68.9×10^{-7}
50-400	65.5×10^{-7}	69.8×10^{-7}
50-500	66.7×10^{-7}	70.7×10^{-7}
50-650	71.2×10^{-7}	74.1×10^{-7}
300-500	69.5×10^{-7}	72.9×10^{-7}
500-650	84.6×10^{-7}	84.3×10^{-7}

4.3. Heating microscope

This analysis permits us to photograph firing body behavior [39-42]. As shown in figure 2, Sanitser formulation presents a firing curve shifted towards lower temperatures, with a greater slope between 1110 °C and 1250°C. After 1250 °C the Sanitser slip shows a trend entirely different from that of the body of VC standard. This behaviour due to the glass effects in the mullite formation [43] and over 1250°C it is possible to see an expansion of the sample certainly due to forming gases. This analysis lets to confirm that Sanitser formulation has a low firing behaviour.

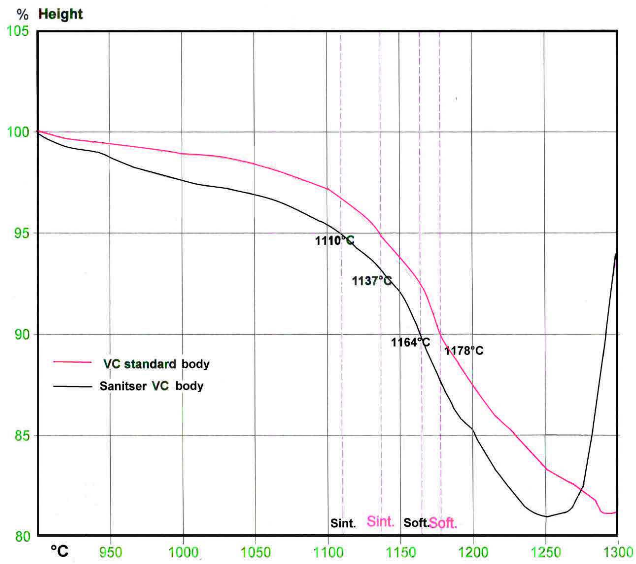

Figure 2. Firing behaviour for Sanitser body compared with standard VC by heating microscope.

4.4. XRPD ((X-ray powder diffraction) analysis

The formation of mullite is conducted, at lower temperatures, to precisely effect the waste glass [43-46]. Therefore, we have verified forming crystallographic phases in Sanitser body through XRPD analysis. This has allowed us to confirm the formation of mullite by the Rietveld method [43-46]. Mullites is synthesized by firing the starting material (Sanitser body) at various temperatures. With this method, it is possible to control quantitatively the amount of crystalline phases and of the remaining amorphous phase. The major phase present after firing is the vitreous phase (from 58% to 63%). The major crystalline phases are quartz (14-18%) and mullite (11-18%). Minor amounts of feldspar (plagioclase) and cristobalite also are present (see figure 3).

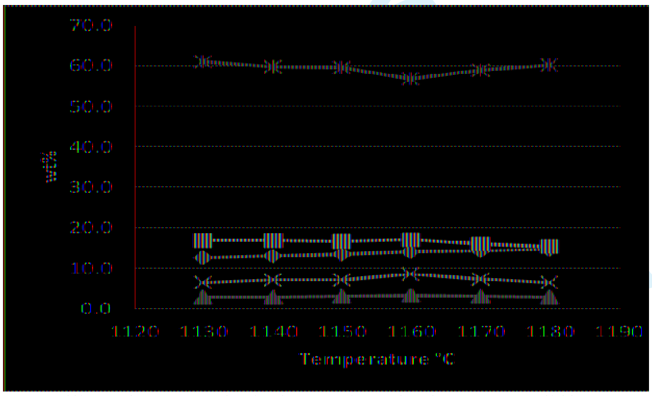

Figure 3. Crystalline phases analysis for Sanitser body (VC) at different temperature

The Sanitser body has a comparable ratio between crystalline phases and amorphous phase, at lower temperatures of about 80°C, than the traditional vitreous china. This ratio, between amorphous and crystalline component, remains almost constant in the entire temperature range explored. This suggests us that transformations occur in the body takes place at temperatures slightly higher to 1110 °C. A detailed analysis of phases shows, in fact, that their contents unchanged from 1120 to 1180°C, except for an increase of mullite and a decrease of other crystalline phases at high temperatures (above 1200 °C).

Pre-industrial test: This is the most important test because it reproduces production conditions and lets to do a comparison between Sanitser formulation and Vitreous China. To realize these trials we casted, glazed and fired about 60 real pieces (wash basin, WC pans and bidet) maintaining same working time and rheological condition used in factory. All casted pieces are sprayed using a low firing glaze, developed specifically for this project, and fired at

1170°C. The kiln present in our pilot plant kilns, according to the type of heating system adopted, is gaseous shuttle kiln. In the kiln is set to a firing curve, shown in figure 4. The firing curve used for the Sanitser slip is of about 17 h, in comparison to that of an industrial cycle that has duration of about 19-22 hours.

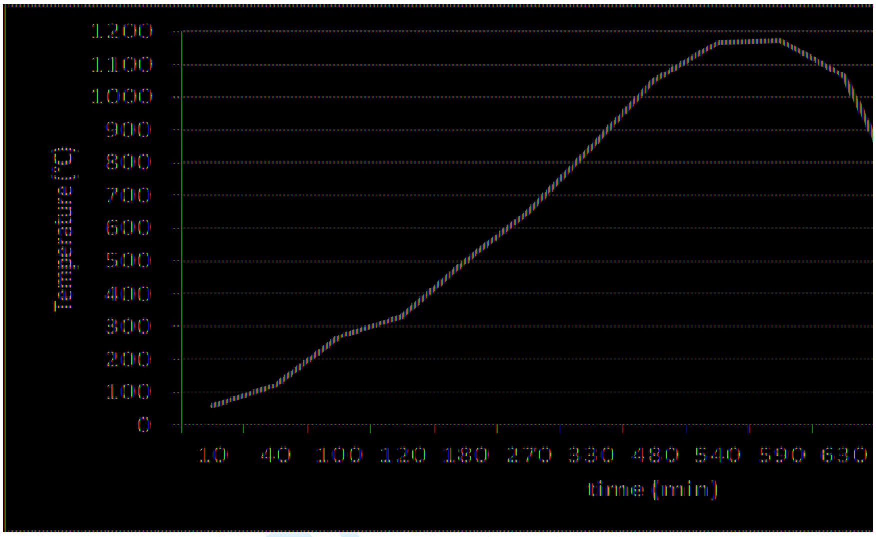

Figure 4. Firing curve used for Sanitser pieces.

The lower firing temperature and a shorter firing cycle confirm that if Sanitser slip is used in industry it would be getting an important decrease of CO_2 and of energy necessary for firing the sanitary ware.

In figure 5 are shown several sanitaryware products obtained in Sanitser project. In pre-industrial production, we did not observe any differences respect to a Vitreous China pieces. Indeed Sanitser raw and fired scraps are comparable to Vitreous china case. Furthermore, it’s important to underline that we realized different shapes to demonstrate Sanitser castability.

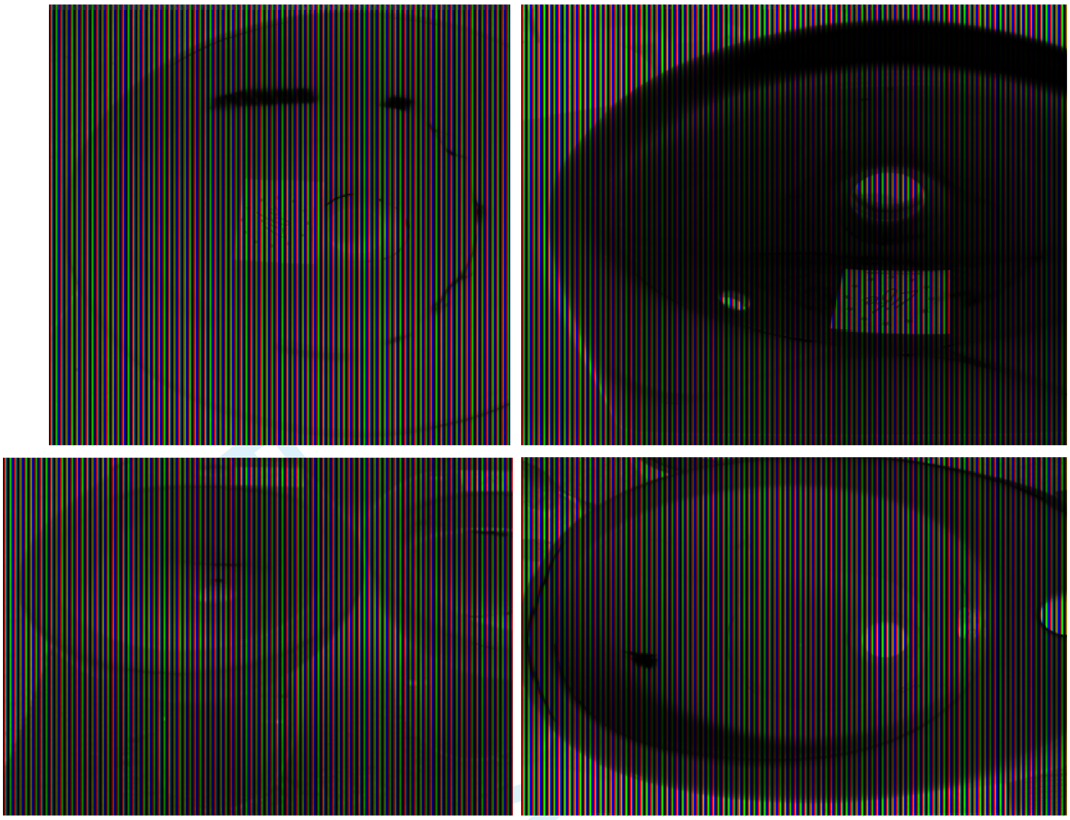

Figure 5. Wash basins, WC pan and bidets produced with Sanitser body.

5. CONCLUSIONS

In this paper, we summarized Sanitser Life project results and we proved that is possible to low vitreous China bodies firing temperature from 1250°C to 1170°C. To get this aim we substituted the feldspar and quartz introducing a blend (supplied by Minerali Industriali srl) in a final percentage of about 43.62% w/w of the total formula.

To confirm these conclusions we make several trials, which allowed us to compare Sanitser formulation with standard VC body. All tests confirm that is possible to low firing temperature without jeopardizing properties normally wanted in sanitaryware. Indeed there are not differences about rheological and mechanical properties, shrinkage and water absorption. Sanitser slip and the pieces held with it overcome EN norms and satisfy industrial parameters. Besides preindustrial trials confirm good results obtained and the next steps involve the industrialization of the Sanitser slip. The novelty of this research isn't the waste glass insertion in ceramic formulas, as today it is used especially in the tile industry, but for the first time we overcome the rheological problems despite the higher percentage of waste glass, amounted to 9.5%.

Also for the first time in a VC body, we have replaced the hard raw materials (quartz and feldspar) with recycled materials with low contents of free silica. This allows to obtain a ceramic body less dangerous to the workers health. Finally a technological level the possibility to bake the VC body at a lower temperature of about 80 ° C, can allow an energy saving and a consequent reduction in CO_2 emissions.

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Body: 01-Mar-2017

Dear Dr. Martini:

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