The use of waste materials in sanitaryware production

The Life Sanitser project was launched in July 2013 as a partnership between four companies: Minerali Industriali, SETE.C., GEMICA and LCE (Life Cycle Engineering). The aim of the project is to design and develop a new kind of vitreous sanitaryware (VSW) body and a new glaze for the sanitaryware industry using recycled raw materials such as soda lime glass (SLG) cullet and secondary raw materials such as scrap granite and fired pieces. The project has two main goals:

a) to introduce recycled and secondary materials into the vitreous sanitaryware body in a percentage of between 15% and 40%; this will enable the body firing temperatures to be lowered by 80-100 °C, thereby reducing production costs;

b) to improve environmental sustainability of the ceramic production process through energy saving, reduction in CO2 emissions and protection of natural resources. Recycled and secondary raw materials, supplied and analysed by Minerali Industriali, will be introduced into the body formulations by Setec, which will have the task of developing a vitreous china body with chemical, physical and rheological characteristics that are identical to those of the traditional body used in the production process but with a firing temperature 80-100 °C lower. GEMICA will be responsible for introducing waste SLG glass and scrap granite into the glaze formulations. Naturally, these formulations must have precise dilatometric characteristics in order to fit properly with the new bodies, as well as specific colorimetric characteristics to ensure an aesthetic result in line with current standards. Replacing quartz and feldspar with scrap glass and granite would allow the firing temperature of the VSW to be reduced from 1230-1250 °C to 1140-1180°C. This would also cut emissions of CO2 in the firing process. The reduction in environmental impact and production costs deriving from the introduction of these new products (body and glaze) will be calculated by LCE by means of a Life Cycle Assessment.

Phase 1: Studying the raw materials to be used in the project

Phase 1 of the Sanitser project involved studying the raw materials to be used in the project and then introducing them into the standard vitreous china body formulations. This was done in a sequence of steps. The first step was to analyse the raw materials to be introduced into the vitre-
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ous china body and glaze in order to eliminate or reduce the percentage of hard materials (quartz and feldspars) in the formulations of traditional ceramic bodies.

This first article provides an initial qualitative analysis of the raw materials of greatest interest to the project. In the next issue of Ceramic World Review we will publish the chemical analyses and the formulations used.

**Quartz** is a vitally important material for the production of vitreous china and is introduced in a percentage of between 20% and 28% by weight. It performs a number of functions:

1. By virtue of its non-plastic nature, it corrects (reduces) plasticity.
2. It increases the whiteness level of the finished product as it normally contains only small quantities of iron and titanium.
3. It allows the coefficient of expansion of the body to be varied.
4. It increases the vitrification temperature of a body.
5. It partially combines with feldspathic glass to form mullite, which together with the residual quartz makes up the mechanical structure of the ceramic body and determines its ability to withstand deformation during firing.

Silica SiO₂ may occur in various crystal forms (quartz, tridymite, cristobalite), but may also exist as amorphous silica. The stability of the various phases depends on the sintering temperature, but this alone rarely gives rise to allotropic transformations. The formation of these phases is also aided by the presence of alkali and alkali earth elements originating from the other phases of the ceramic body, while particle size also has a big impact on the reaction kinetics of the quartz fraction.

Of all the possible transformations of quartz, the one that is of industrial interest is the transition quartz α→β, which occurs at 573 °C with an abrupt change in volume. If this does not occur uniformly over the entire volume of the piece, it may result in breakage of the ceramic body. This aspect has a major impact on the sanitaryware firing and re-firing curve.

The quartz selection criteria are:

- Silica content > 96%.
- Alkali content < 0.2%.
- Fe₂O₃+TiO₂ content < 0.2%.
- Alkali content < 0.2%.

The quartz particle size distribution curve is another important factor to consider. In particular, the quantity of particles larger than 60 µm should be low (<2%). Conversely, an excessive particle fineness may affect the rheological properties of the slip during the casting process, as well as the thickness forming time and body shrinkage.

**Feldspars**, or fluxes, serve to lower the vitrification temperature of bodies as they form a vitreous phase at a much lower temperature than would otherwise be possible. Fluxes promote vitrification of vitreous china bodies and reduce their porosity. During firing, the vitreous mass created by the fluxes has a twofold action:

- It interacts with free silica and with the clay materials, facilitating the process of melt formation.
- It closes the pores in the ceramic body, thereby increasing its density and compactness.

Due to their non-plastic nature, the fluxes in the liquid slip display similar behaviour to that of quartz, in other words they act as leaning agents.
The fluxes most widely used in industry are feldspars and feldspathoids, which are normally used in quantities of between 15% and 22% of vitreous china bodies. Potassium feldspar is currently considered the ideal flux for ceramic as it has a very wide melting range. And the wider the melting range the greater the firing uniformity in fired pieces. This has considerable advantages as the high viscosity of the potash glass allows for a high degree of vitrification without the risk of product deformation during the firing stage. Whereas potassium feldspar melts at 1150 °C, pure sodium feldspar melts at 1118 °C to form a less viscous glass with a narrower melting range than potassium feldspar. One factor that plays a fundamental role in determining the transformation temperatures of a feldspar is its particle size distribution: finer particles shift the firing curve towards lower temperatures. It is advisable for 40-55% of feldspar particles to be smaller than 10 μm. To ensure a good white colour, the Fe₂O₃ + TiO₂ content should not exceed 0.3%. To choose whether to use a sodium feldspar or a potassium feldspar, two characteristics should be considered:

- Sodium feldspar ensures good vitrification at lower temperatures than potassium feldspar.
- Potassium feldspar gives the body greater resistance to deformations over a wider temperature range than sodium feldspar.

In particular, bodies with potassium feldspar have a vitrification range of about 50 °C compared to 25-30 °C with sodium feldspar. It should be stressed that all the characteristics of feldspars during firing are affected in terms of intensity and kinetics by the size of the particles, especially in the case of rapid cycles with high heating rates.

In ceramic sanitaryware production a 5-8% percentage of defective fired vitreous china pieces are used (ground and reintroduced into the bodies without modification), taking the name of pitcher. This ceramic scrap is introduced into the vitreous china bodies as a partial substitute for the quartz. Its use is often justified by economic and environmental considerations. By using industrial waste in the production cycle, it is possible to reduce disposal costs and to partially replace more expensive materials. However, the use of this material is also beneficial from a technological viewpoint:

- As ceramic scrap consists of ground waste, it also contains the glaze that covered the pieces and is therefore not completely inert. Consequently it has a slight fluxing action that allows the feldspar content of the body to be reduced while maintaining the same degree of vitrification.
- Due to its high alumina content (23-24% by weight), the introduction of ceramic scrap into the body allows the vitrification/deformation ratio to be optimised, if used to suitably replace quartz and feldspar.
- By using scrap in place of a portion of the quartz it is possible to vary the coefficient of expansion of the body and above all to mitigate the negative impact of a α→β quartz transformation, especially in the case of rapid firing cycles.
- The choice of suitable particle sizes and quantities of chamotte may enable the rheological properties of the slip and the casting times to be partially adjusted.

Nella barbottina liquida i fondenti, essendo non plastici, hanno un comportamento simile a quello del quarzo, agiscono cioè da smagranti.

I fondenti più usati nell’industria sono i feldspati e i feldspathoidi, solitamente impiegati in quantità variabili dal 15% al 22% negli impasti di porcellana sanitaria. Il feldspato potassico è a tutti’ogni considerato il fondente ideale per la ceramica perché è caratterizzato da un intervallo di fusione molto esteso, e, maggiore è l’intervallo di fusione del feldspato, maggiore è l’uniformità della cottura nei pezzi cotti. I vantaggi sono notevoli, in quanto l’alta viscosità del vetro potassico permette di ottenere elevati gradi di vitrificazione senza il rischio di fenomeni di deformazione del prodotto in fase di cottura.

Il feldspato potassico puro è caratterizzato da una fusione a 1150 °C mentre il feldspato sodico puro fonde a 1118 °C, dando un vetro meno viscoso, caratterizzato da un intervallo di fusione più ristretto rispetto al feldspato potassico. Un fattore che gioca un ruolo fondamentale nella determinazione delle temperature di trasformazione di un feldspato è la sua distribuzione granulometrica: particelle più fini spostano la curva verso temperature più basse. È consigliabile che un feldspato abbia dal 40-55% delle sue particelle più piccole di 10 μm. Il contenuto in Fe₂O₃ + TiO₂ non dovrebbe superare lo 0,3% per garantire un buon colore bianco.

Per scegliere se usare un feldspato sodico o un potassico occorre considerare due caratteristiche:

- Il feldspato sodico garantisce una buona greificazione a temperature più basse rispetto al feldspato potassico;
- Il feldspato potassico, rispetto al sodico, conferisce all’impasto una maggiore resistenza alle deformazioni in un più ampio intervallo di temperatura.

In particolare, impasti col feldspato potassico possiedono un intervallo di vitrificazione pari a circa 50 °C, valore che si riduce a 25-30 °C se il feldspato è sodico. È bene ribadire che tutte le caratteristiche dei feldspati in cottura sono condizionate, nell’intensità e nella cinetica, dalla granulometria delle particelle, soprattutto se si parla di elevata velocità di riscaldamento e quindi di cicli rapidi.

Nella produzione di ceramica sanitaria, si utilizza una percentuale variabile dal 5-8% di pezzi cotti di vitreous china difettati (macinati e reintrodotti come tal quale negli impasti), che prendono il nome di pitcher. Il rottame ceramico va inserito negli impasti di vitreous-china in parziale sostituzione del quarzo. Il suo impiego è spesso giustificato da ragioni di ordine economico, ma anche ecologico: si tratta infatti di un riutilizzo nel ciclo produttivo di uno scarto industriale che permette non solo di risparmiare i costi di smaltimento, ma anche di sostituire parzialmente materiali più costosi. In realtà, l’impiego di questo materiale è interessante anche per altri motivi di natura tecnologica:

- Il rottame ceramico non è un materiale completamente inerte in quanto, essendo costituito da scarti mcaminati, contiene anche lo smalto che rivestiva i pezzi; possiede quindi una leggera azione fondente che può consentire di diminuire il contenuto di feldspati nell’impasto a parità del grado di vitrificazione.
- L’introduzione del rottame ceramico nell’impasto, grazie all’alto valore del contenuto di allumina (23-24 wt%), permette di ottimizzare il rapporto greificazione/deformazione, se opportunamente sostituito al quarzo e al feldspato.
- L’impiego di rottame al posto di parte del quarzo permette di variare il coefficiente di dilatazione dell’impasto e soprattutto di attenuare l’effetto della trasformazione quarzo α→β e i relativi effetti negativi soprattutto nel caso di cicli rapidi di cottura.
- La scelta delle granulometrie e quantità di chamotte adatte può consentire di regolare parzialmente le proprietà reologiche della barbottina e i tempi di colaggio.

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