AN INDUSTRIAL APPROACH TO CERAMICS: SANITARYWARE

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PRODUCTION PROCESS FOR SANITARYWARE

World sanitaryware production is estimated to have grown by 61.3% from 216.6 to 349.3 million pieces over the decade 2004-2014, corresponding to a compound annual growth rate of 4.9%.

Asia, the largest production area with 172 million pieces in 2014 (85% growth since 2004), further increased its share of total production over the decade to almost 50%. However, the most significant growth was in Africa (+300%), the Middle East (+181.7%), and South America (+163.7%), the latter region driven by Brazil as the world's second largest producer country (24 million pieces).

In a context of steady globalization of production and markets, the negative figure for the EU and NAFTA regions hardly comes as a surprise, with production volumes dropping over the decade by 3 and 6 million pieces respectively. This is despite the fact that in the NAFTA region Mexico has almost tripled its volumes, which are now estimated at 18 million pieces.

World sanitaryware production is also increasingly concentrated in the hands of a few very large multinational groups. It is estimated that in 2014 the top 20 groups (excluding those in China) have produced over 43% of total world production.

In this paper we examine the materials most commonly used in the manufacturing of sanitaryware in porcelain, fire clay, and fine fire clay (Mariani, 1974; Fortuna & Caponi, 1987; Reed, 1988; Fortuna, 2000).

For sanitaryware porcelain bodies, the materials normally used are kaolin, clay, feldspar or feldspathoid, quartz, and ground fired waste. Another ingredient is chamotte, used in fire clay bodies that are made up of fired and ground refractory clay (Mariani, 1974; Fortuna & Caponi, 1987; Reed, 1988; Fortuna, 2000).

The sanitaryware porcelain and fire clay glazes are mainly made up of quartz, feldspar or feldspathoid, kaolin, earth alkaline metal carbonate, and zinc oxide. The opacifiers used are zirconium silicate and rarely, due to its cost, tin oxide. The engobe used almost only in the production of fire clay is made up of the raw materials used in sanitaryware porcelain bodies, however in different proportions.

The production cycle normally used in the vitreous china or fire clay sanitaryware industry is reported in the following chapters (Fig. 1).

The body preparation

The preparation process of a body is essentially as follows (Fortuna & Caponi 1987; Sacchiero, 1987; Kohut, 1992; Fortuna, 2000).

a) First phase dissolving. Clays, together with water and deflocculants, are placed into a dissolver. The working time with these dissolvers varies from 3 to 4 hours, depending on the type of clay. The total amount of deflocculant necessary for the body should be used as much as possible in this first dissolving phase, as it is well known that the same amount of deflocculant added in different ways causes a different rheological behaviour of the slip. The deflocculant to be used generally varies from 0.1 to 0.5% in dry weight of the body depending on the slip formulation and the fluidifying agent used. Other deflocculants more commonly used are sodium carbonate and barium carbonate.

b) First phase sieving and de-ironing process. Before being transferred to the second phase dissolving, the clay dispersion is screened using vibrating screens with one or more meshes that vary from 125 to 90 micron. This operation becomes necessary in order to eliminate impurities present in the material, even when purified clay blends are used. The sieved slip is passed through electromagnets and/or permanent magnets that can be fixed directly under the sieve. Their function is to detract any contaminating magnetic material that could be
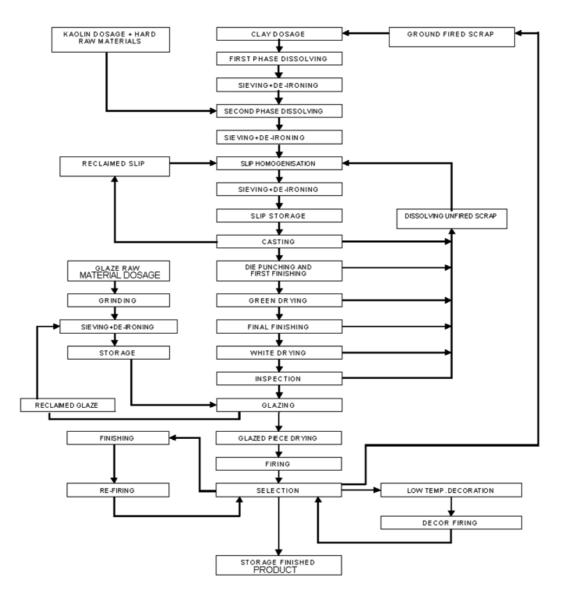
present (iron) from the body.

Fig. 1 - Sanitaryware process scheme.

c) Second phase dissolving. Normally this is a dissolver with a marine propeller-type stirring device in octagonal cement tank. The first phase clay dispersion, quartz, feldspar kaolin and, if used, chamotte are placed in sequence into this dissolver. A turbo blunger may be used in alternative.

d) Second phase sieving and de-ironing process. The process examined in point b) is repeated. In this case however, the screen's mesh is usually bigger, the larger the size of the quartz and feldspar grains compared to clay and because the greater specific weight and the lesser fluidity of the slip could make sieving with small mesh complicated. Mesh varying from 125 to 180 micron are used.

e) Dissolving of unfired scraps and casting recovery slip. This operation is carried out in a normal dissolver or a turbo blunger. Water, unfired scraps and the recovery slip are added together with barium carbonate to precipitate the sodium and calcium sulphates contained in both the unfired scraps and the slip, followed immediately by the moulds being attacked by deflocculants and by the dissolution of plaster.

f) Sieving and de-ironing process of the recovery slip. Proceed as seen in point d).

g) Mixing of the final slip. This operation is carried out in a pit fitted with a mechanical paddle stirrer that has a paddle rotation speed of approximately 12÷16 rpm. Once the body is homogenized, its main characteristics are checked: *i*) specific weight; *ii*) viscosity; *iii*) thixotropy; *iv*) pH; *v*) temperature.

Adequate corrections are made if necessary always trying to avoid the addition of deflocculants and/or water. It is preferable to modify the body characteristics by adding a slip with the suitable physical properties. When the principal body parameter values fall within the pre-set standards, the slip is transferred to the storage tanks.

Casting

There are different types of casting available. Some of the types are normal bench casting, battery casting for sanitaryware, beam casting, low pressure casting and high pressure casting for sanitaryware (Vouillemet, 1986, 1992; Hogg, 1986; Paganelli, 2006). The process of casting is the same in all types of casting (Fig. 2): slip is poured into the mould and allowed to form casting layer on the mould. Then the excess slip is drained through drain hole. Now casted ware is allowed to dried and then released from mould. In this stage the ware is known as green ware. This green ware is allowed to dry in atmospheric temperature for one to three days before sent to drier. Before sending to drier this green ware is finished to smooth joint edges, repair small cracks, small pin holes, bad finishing and once this ware is ready it will be sent to drier for drying. Moisture content of the green ware before drier will be varying from 22% to 12%.

Fig. 2 - Casting sanitaryware industrial process.

Drying

Green piece form casting will be sent to Control and spraying through Drier. In Drier, Green MOR of the ware is improved by removing the mechanically combined water from ware. Moisture content of green ware after drier will be varying from 1.5% to 0.5%. Drying process will take from 6.5 hour to 12 hrs. Drier may be batch drier or tunnel drier. Batch drier will be loaded at once and unloaded at once. Tunnel drier will be fed continuously with ware and continuously unloaded at other end. Gradual heat will be done from atmosphere temperature to 110 °C to 120 °C. During this process ware will loss his weight and shrink in size.

Inspection and glazing

Defected wares will be repaired or rejected depends upon the defects. Normally control and spraying department will be handled by same team. Properly checked ware will be sent to spraying are for spraying.

Glaze, used for spraying the sanitaryware, will be done by manual methods or robotic methods. In spraying 0.8 mm to 1.6 mm thickness of the glaze is applied on the wares as per the requirement. Once spraying done allowed some time to dry for few minutes.

Firing

Sprayed ware will be loaded in kiln car. Dust and other impurities are removed from ware by air blower or vacuum. Kiln maximum temperature will be 1250 °C.

Different types of kiln can be used in firing (shuttle kiln, tunnel kiln). Sanitary ware kiln (Fig. 3) have three zones, pre-heating, firing and cooling zones. In pre-heating zone mechanically and chemically combined water has been removed from the ware. At firing zone all the raw material are fused together and glaze are fused evenly. At cooling zone sudden cooling is done to create glossy surface. Once product fired, it will be moved to sorting area.

Fig. 3 - Ceramic kiln for sanitaryware.

Final selection

In this stage of the process all wares from the kiln are inspected and sorted according to the defects. If ware is defects free then it will be send to packing section for packing. If ware has minor defects like pinholes then it will be repaired by cold fill. If has light glaze or wavy or blib then it will be sent to refire section. If there is a crack it will be rejected. This quality check is very important to maintain standards. And also random sampling will be made for flush test, smoke test, leak test and load test.

Refiring

All repair wares will be send to rework section for minor repairs. All ware are required according to the defect and sent to tunnel kiln. Once repaired and fired again it will be inspected and again separated as per the

grade. If quality standards are met then it will sent to packing. If needs repairing again it will repaired in refire section. Major and un-repairable wares will be sent to rejected area. These are normally warpage or cracked pieces.

Packaging

It is the final stage of sanitary ware manufacturing/production process. All sanitarywares that are passed quality standards are packed and dispatched to ware house.

RAW MATERIALS USED FOR CERAMIC BODIES

Clay and kaolin

Clays are fundamental for both sanitaryware porcelain and fire clay sanitaryware bodies (Bourgy & Lymath, 2017), as they make up the properties that are indispensable for manufacturing and, in particular: *i*) plasticity and workability during cast moulding, *ii*) mechanical resistance before-firing, *iii*) contribute to the vitrification of the body during firing.

Kaolins are introduced into the body (Sheppardson, 2011) to give it the necessary plasticity and workability as already mentioned for clays. However, the partial substitution of clays for kaolins improves the whiteness of the bodies, increases the alumina rate and therefore improves its resistance to deformation at high temperatures.

Quartz and feldspar

Quartz is a material of primary importance (Weiss, 1979), as it is introduced in the vitreous china body in percentages that vary from 20 to 28%. On the other hand in the fire clay slip lower percentages are used, usually between 10% and 16%. The action that quartz has on the two types of bodies, even in different measures, can be summarized as follows: *i*) it corrects plasticity; being a non-plastic material, it reduces plasticity; *ii*) it increases the whiteness of the finished product, given that it normally only contains small quantities of iron and/or titanium; *iii*) it makes it possible to vary the body's expansion coefficient; *iv*) it increases the body's vitrification temperature; *v*) 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.

The feldspar is silica-aluminates of alkaline metals and/or earth alkalines (Smith, 1974), the most important for the sanitaryware industry being orthoclase and albite.

The natural feldspars used in the industry are never pure and are often a combination of the two above-mentioned types with the addition of secondary materials such as anorthite and quartz.

Potassium feldspar is today still considered to be the ideal flux for vitrified paste products as it gives a very viscous glass characterised by a very long melting range. This has several industrial advantages: *i*) the high viscosity of potassium glass can obtain high degrees of vitrification without the risk of provoking evident deformation phenomena of the product during firing; *ii*) often in the various areas of the same section of an industrial kiln (especially between the higher and lower sections) there are considerable differences in temperature. In pieces such as sanitaryware appliances that can be over 600 mm in height, this could result in considerable differences in vitrification in the various parts of the same piece. This phenomenon is even more reduced where the melting range of feldspar is greater.

Pure potassium feldspar is characterised by incongruent melting at 1.150 °C; this is only theoretically important as it is not possible to obtain materials such as pure feldspar at an industrial level. Pure sodium feldspar melts congruently at 1.118 °C, resulting in a less viscous glass characterized by a shorter melting range compared to potassium feldspar.

Feldspathoids and other fluxes

In the sanitaryware industry other fluxes with particularly valuable technological characteristics are often used (Williamson, 1980; Holdridge & Ryder, 1962), or when these are easily available at low cost. The most

important are nepheline-syenite and pegmatites. Nepheline-syenite is a natural material made up of nepheline, a feldspathoid found in syenite rocks. It is characterised by a high alkaline oxide content (from 15 to 17%) and by a higher alumina percentage (around 24%) than what is found in composes other fluxes (Edgar, 1965).

This particular chemical composition gives this material the characteristics that make it optimal for vitrified porcelain sanitaryware production especially at rapid cycles. In fact, the high alkali content allows for the vitrification of bodies at relatively low temperatures, as with albite. On the contrary to albite though, nepheline-syenite gives bodies with a greater vitrification range (Edgar, 1965). Furthermore, the glass generated by nepheline is very viscous and considerably reduces the entity of deformation thanks to its high alumina content that on the contrary occurs in a sodium feldspar body. Nepheline-syenite therefore, at least at the temperatures used for sanitaryware production, combines the advantages of albite and of orthoclase, with an added high moistening potential at the molten state that allows for the intimate contact with the particles of other body components, also giving them an easier attacking and dissolution potential. The only disadvantage of this material is its high cost.

Pegmatites are natural blends of quartz and sodium and/or potassium feldspar often with minor to accessory clay minerals. Their behaviour during firing is similar to that of feldspars containing the same alkaline oxides, for their high SiO_2 content (also above 85%) and for the low quantities of very high melting temperature alkali fluxes. The use of pegmatite as a flux in a body leads to the almost complete substitution not only of the feldspar but also of the quartz. This material is normally used only in countries where it is readily available and where it is of good and constant quality (*e.g.*, Germany). In fact, natural pegmatites are often characterized by a considerable variability of the chemical-mineralogical content and therefore of their technological characteristics.

Chamotte

This term normally refers to both calcined and ground clay that represent almost totally the non-plastic part of fire clay bodies, and vitreous china waste or ground fire clay that is then reintroduced as such into sanitary porcelain or fire clay bodies.

Chamotte is introduced into vitreous china bodies as a partial substitution of quartz and feldspar. Its use is often justified by economic and increasingly, by ecological reasons. This is in fact a re-use of industrial waste in the production cycle that not only cuts disposal costs, but also partially replaces the more expensive materials in the bodies. These are not the only reasons that promote the use of this material, in fact: *i*) chamotte is not a completely inert material as it is made up of ground waste and contains even the glaze that coats pieces. It therefore has a light fluxing action that can reduce the feldspar content of the body with the same vitrification rate; *ii*) b) the introduction of chamotte into the body, thanks to its high alumina content (23-24% on average), optimizes the vitrification/deformation ratio if appropriately substituting quartz and feldspar; *iii*) the use of chamotte in the place of part of the quartz varies the expansion coefficient of the body and above all it minimizes the effect of the quartz-alpha quartz-beta transformation and the relative negative effects especially in rapid firing cycles; *iv*) the choice of suitable granulometry and the quantity of chamotte can partially adjust the rheological properties of the slip and the casting time. In some cases, vitreous chamotte is introduced also into fire clay bodies.

Chamotte for fire clay

This chamotte is produced by calcining kaolins or alumina rich clays at high temperatures mostly in rotary kilns. After firing, the chamotte is ground and then sieved. Firing determines, above all, the final porosity of the chamotte. This is very important as it changes the water quantity of the body and therefore the specific slip weight and its shrinkage. The types of chamotte normally used in the sanitaryware appliance industry have a water absorption that varies from 3 to 7%. Grinding must be carried out by machine that produce particles with edges, least rounded possible. Sieving is very important because it conditions the chamotte's granulometric distribution that considerably influences the bodies. In fact, finer particles result in: *i*) the need for more body

water and therefore greater unfired and fired shrinkage; *ii*) greater mechanical resistance of the fired body; *iii*) an increase in fired deformation; *iv*) a reduction in the porosity of the fired body; *v*) less resistance to thermal shock; *vi*) better surface quality of the unfired product, that almost always makes the application of an engobe unnecessary, and an increase in quality due to the significant reduction of defects such as grains and black spots on the finished product.

SANITARY WARE BODY

The composition of bodies, and also of glazes, must be studied in order to obtain a suitable compromise for all the production phases. In fact, many defects and production problems depend precisely on these production phases. Vitreous china bodies are normally made up of ball clays, kaolins, quartz and feldspars or other fluxes, such as nepheline, in the following percentages: *i*) 20÷28% ball clay, *ii*) 25÷35% kaolin, *iii*) 17÷31% quartz, and *iv*) 15÷23% feldspar or other fluxes, Moreover, 3÷9% of ground fired scraps is almost always introduced into the formulation of the body in partial substitution of other components or as extra base additions. The addition of this material is not only made for economic reasons (chamotte costs 20÷30% less than the raw materials), but also for technological reasons such as: *i*) an addition of chamotte actually reduces the thickness formation time, with all other conditions remaining the same; *ii*) if used to partially substitute quartz and other materials, maintaining unaltered the other fundamental parameters of the fired body (shrinkage, deformation, water absorption), it reduces the thermal expansion coefficient and, in particular, attenuates the effect of the quartz-beta quartz-alpha transformation during the cooling phase. The latter is extremely important especially when the aim is to reduce firing cycle times.

Controlling the main slips characteristics

Controls carried out on a slip are fundamentally important as they guarantee the maximum constancy value of all the technological characteristics that, as we shall see, greatly influence the entire production process (Fortuna, 1992; Pozzi & Galassi, 1994). These controls must be carried out on both the newly prepared slip and the slip that is sent daily to the casting department. Controls of the following parameters are made: *i*) specific weight; *ii*) temperature; *iii*) viscosity; *iv*) thixotropy; *v*) thickness formation time.

In Table 1 are reported the standard industrial range parameters for vitreous china slip. As previously seen, the fire clay body preparation process is the same as for a vitreous body, at least as far as the order of operations is concerned.

Table 1: Physical characteristics of sanitary porcelain slips.

SPECIFIC WEIGHT:	1.80÷1.85 Kg/dm³ (contained in solids equal to 72÷75%)
Gallenkamp VISCOSITY:	290÷320°
Brookfield VISCOSITY:	6÷8 Poise
Gallenkamp THIXOTROPY:	30÷40° (after 1 min)
Brookfield THIXOTROPY:	70÷90 Poise (after 1 h at 2 rpm)
pH:	8÷9
TEMPERATURE:	18÷25 °C

As regards the dissolving phases of the clay dispersion and its sieving and de-ironing process, the description used for a vitreous body is valid here also. The exception is in the water content (less in the case of fire clay): from 28÷25% in weight for vitreous to 20÷22% for fire clay or fine fire clay. Normally the deflocculants are also the same, even though their dosage may obviously vary. In Table 2 are reported the standard industrial range parameters for fine fire clay and fire clay slips.

Table 2: Physical characteristics of a fire clay or fine fire clay slip

	FIRE CLAY	FINE FIRE CLAY
Specific weight in Kg/dm³	2.00 ÷ 2.05	1.95 ÷ 1.97
Brookfield viscosity in Poise	18 ÷ 20	15 ÷ 18
Content of solids (% in weight)	80 ÷ 78	74 ÷ 76
Gallenkamp viscosity in degrees	180 ÷ 200°	190 ÷ 220°
Gallenkamp thixotropy in degrees	40 ÷ 50°	30 ÷ 50°

REFERENCES

Bourgy, L. & Lymath, G. (2017): New kaolins and Ball Clays to Increase Sanitaryware Body Performances. *Ceram. Forum Int*., **94**, 5-10.

Edgar, A.D. (1965): The Mineralogical Composition of Some Nepheline Alteration Products. *Amer. Mineral*., **50**, 978-989.

Fortuna, D.M. (1992): Le barbottine da colaggio nell'industria del sanitario. *Ceram. Inform.*, **319**, 593-601.

Fortuna, D.M. (2000): Sanitaryware. Ed. Faenza, Faenza, Italia.

Fortuna, D.M. & Caponi, V. (1987): La fabbricazione degli apparecchi igienico-sanitari nelle industrie del comprensorio di Civita Castellana. ENEA-Centro Ceramico Civita Castellana, Italia.

Hogg, S.C. (1986): Confronto tra la colatura dei sanitari sotto pressione e colatura tradizionale in stampi, con particolare riferimento alle proprietà delle argille. *Ceramurgia,* **16**, 69-74.

Holdridge, G.A. & Ryder, S.H. (1962): Norwegian, Nepheline Syenite. *Transaction Eight lntemational Ceramic Congress* (Copenhagen), 355-366.

Kohut, W. (1992): Deflocculant studying the sanitaryware industry. *Am. Ceram. Soc. Bull*., **71**, 943-947.

Mariani, E. (1974): Chimica applicata ed industriale. UTET, Torino, Italia, 1115 p.

Paganelli, M. (2006): Le applicazioni pratiche della reologia nell'industria ceramica. *In*: "Reologia applicata alla ceramica", Società Ceramica Italiana ed., S.A.L.A. srl., Modena, Italia, 63-102.

Pozzi, P. & Galassi, C. (1994): La reologia dei materiali ceramici tradizionali, Ed. Faenza S.p.A., Faenza, 203 p.

Reed, J.S. (1988): Principles of ceramic processing. John Wiley & Sons, New York, USA, 688 p.

Sacchiero, E. (1987): Casting with Medium Pressure. Chemical Abstracts 85:165496j, *Interceram*, **1**, 33-35.

Sheppardson, P. (2011): Advances in Test Methods for Designing Optimised Ceramic Blends from a Raw Material Supply Perspective. *Ceram. Mat.*, **63**, 233-238.

Smith, J.V. (1974): Feldspar minerals. Vol. 1 - Crystal Structure and Physical Properties. Springer Verlag Gmbh Freiburg, Germany, 627 p.

Vouillemet, M. (1986): Le coulage. *L'Industrie céramique*, **803**, 172-179.

Vouillemet, M. (1992): La filtration des barbotines de vitreous sanitaire. *L'Industrie céramique*, **876**, 745-751.

Weiss, A. (1979): The raw matenal quartz and its preparation. Ceramic Monographs-Handbook of Ceramics, **28 (3)**, Verlag Schmid Gmbh Freiburg, Germany.

Williamson, W.O. (1980): Feldspathic or feldspathoidal fluxes and their beneficiation. Ceramic monographs-Handbook of Ceramics, Verlag Schmid Gmbh Freiburg, Germany.