BUBBLE CONTROL IN CERAMIC GLAZES

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ABSTRACT

In the framework of an international co-operative research project of porcelain and tile manufacturers, raw materials suppliers and ceramic institutes within the GROWTH program (5th Framework program) research was performed on bubble control in ceramic glazes. The project included a literature inventory of relevant mechanisms, parameters and cause-effect relations. A short overview, by discussing the present state of the knowledge on bubble genesis, growth and related defects, primary and secondary causes for bubble defects and parameters of influence will be presented. The conclusions regarding the bubble defects are discussed, indicating the different views on issues yet under discussion, like bubble movement and the origin of bubble content.

A classification matrix for bubble defects and a relation matrix for causes and influencing parameters have been developed. The inventory and the matrices have been the basis for the development of a database on glaze defects. The concept of the database and its use in ceramic production are shown.

To be able to define relevant glaze characteristics a combination of test methods has been developed to specify the glaze in relation to its behaviour regarding bubble growth. Parameters like porosity of the glaze, sealing temperature and viscosity of the glaze have been taken into account. A numerical model has been developed describing the mechanism of bubble generation and bubble growth, which was validated by laboratory testing. General conclusions are presented.

On this basis the possible control actions for different ceramic glaze types have been defined and tested on laboratory scale and in production situations. The use of additives to the glazes as improvement possibility has been tested for the different glaze systems, leading to the definition of different additives usable for different glazes. The results of prepilot and pilot tests of improvement possibilities have been used to conceive a general glaze improvement routine, based on classification and characterisation by the developed methods. The results and the improvement routine using the inventory, the database and the numerical model will be presented, as well as a technological concept for glazes with controlled bubble growth. Possible future implementations of the project results will be discussed.

1. INTRODUCTION

The quality of glazed products manufactured in the ceramics industry is dependent on the outer surface of the product. Both the aesthetic and mechanical properties of the ceramic product are determined by the amount and size of defects in the surface layer. Unfortunately, defects, in particular bubbles, often are difficult to avoid in the ceramic glaze. The reject rate during the production of ceramic products can be quite high (up to 11%) due to these defects in the glaze layer. Therefore a international co-operative research project within the GROWTH program (5th Framework program) research was performed on bubble control in glazes for ceramic products (acronym: BUCOGLACER) by porcelain and tile manufacturers (Mosa Porcelain & Goedewaagen Gouda BV (Netherlands), Porcelanas Bidasoa (Spain), Thun (Italy), Bernhard Link GmbH (Germany)), a supplier of glazes for the ceramic industry (Rheinische Email u. Glasurenfabrik Mondré & Manz GmbH (Germany)), and ceramic institutes (FGK (Germany), TNO TPD (Netherlands)), sponsored by a *glaze, body and ceramic raw materials supplier (Imerys Tableware (France))* and a supplier of ceramic raw materials and bodies (WBB Fuchs (Germany). The project takes an integral approach to the understanding and control of the excessive generation of bubbles and the life of bubbles during the firing process, and aims at control of the bubble growth and prevention of bubble defects by preventive process measures, optimised process settings and new technologies to reduce the reject rate due to bubble defects by at least 50 %. The background of this approach is defined by the high reject rates, the missing uniform basis for defect classification, the trial & error character of the present knowledge on glaze defects and the need for an overall process approach for tackling the bubble defects by interlinking the knowledge on raw materials, glaze and the process conditions.

The work carried out covers the following tasks, which will be successively addressed:

- the inventory of knowledge pinholes and process conditions and transference into a database
- the physical/chemical characterisation of materials and processes
- physical/chemical description of bubble generation and development
- development of process conditions to control bubble formation
- performance of pre-pilot and pilot tests

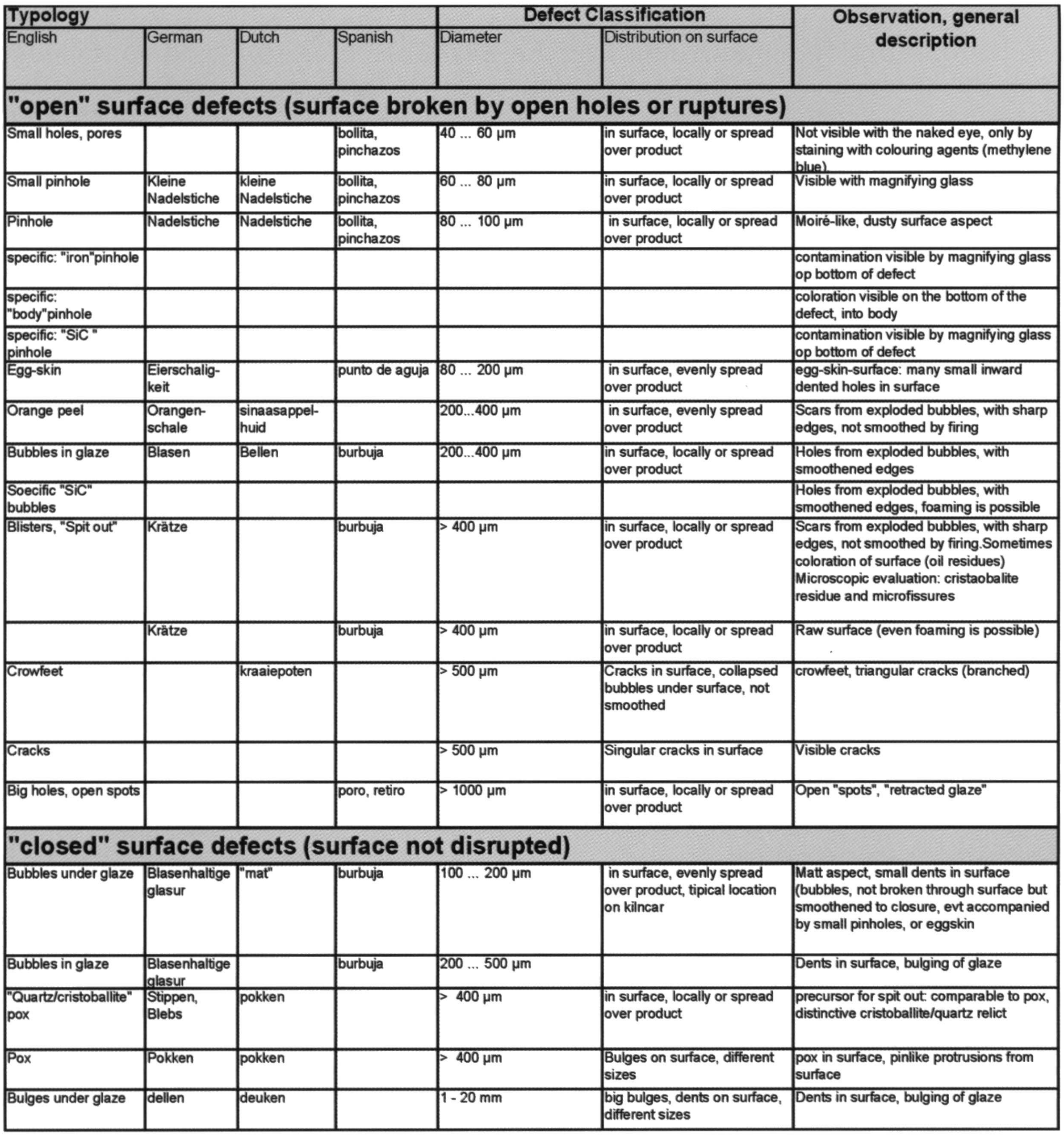
Due to the wide scope of the project the main aspects and results will be discussed. Some technical results are not yet publishable, and therefore will not be specified in detail.

2. THE INVENTORY OF KNOWLEDGE PINHOLES AND PROCESS CONDITIONS AND TRANSFERENCE INTO A DATABASE

An extensive inventory on of relevant mechanisms, parameters and cause-effect relations has been performed using open literature and interviews with experts to prepare a topic-based overview of the knowledge on bubble defects, a literature reference list, as well as a defect classification matrix and a matrix ranking process parameters of influence. Main conclusions derived by structuring the available literature and knowledge from the interviews of the participants, which have been used for further investigation, structuring of the database and the modelling of bubble generation and growth are:

- Glaze layers can be regarded as non-ideal silicate glass systems, but have specific characteristics due to their heterogeneous nature (containing air enclosures, crystals, recrystallisations, opacifiers, pigments, chemical inhomogeneities) and their reaction with the ceramic body.
- The generation of bubbles is indicated to be inherent to the ceramic glaze-body system: reactions at the interface increase the acidity of the melt, and lead to changes in the solubility of different components, causing bubble formation.
- Causes for bubbles and bubble defects can be divided into primary (inclusion) causes and secondary causes (reactions and transitions during firing). Causes for bubbles however not always have to lead to detectable defects.
- The bubble size distribution can be bimodal, defined by the mentioned primary causes (in the glaze) and the secondary causes (the glaze-body interface).
- The growth of bubbles in the ceramic glaze depends on:
  - Solubility of components, changes from chemical to physical solubility and the solubility as a function of temperature.
  - Diffusion of components, influenced by partial pressures, concentration gradients, and diffusion constants as a function of temperature.
  - Surface tension of the glaze, influenced by local composition and temperature.
  - The viscosity of the glaze, influenced by local composition and temperature.
- The movement of bubbles under the influence of gravity is often contradicted, but calculation for the relevant viscosity, bubble sizes, and temperature-time treatment indicate possible movement for bigger bubbles (> 100 μm). Movement based on surface forces is described.
- The interpretation of bubble content analysis is to be done with caution: diffusion and sample preparation can influence the content and the analysis, so the indication of the cause is lost. "Freezing" of samples can be used. The problem is illustrated by the contradictive explanation of the high nitrogen content of bubbles. Some authors indicate that after firing the bubble content will tend to equal the kiln atmosphere. No indication however can be found for this effect.

A classification matrix has been conceived to create a necessary uniform basis for defect classification, while primary and secondary causes are indicated for the defects. Defects are classified using the criteria of size and distribution over the surface; the size and distribution of the underlying bubbles and the aspects open or closed surface disruption. In figure 1 an excerpt of the classification matrix is shown, defining the initial classification, as well as the typology reference.



Typology				Defect Classification		Observation, general description
English	German	Dutch	Spanish	Diameter	Distribution on surface	
"open" surface defects (surface broken by open holes or ruptures)						
Small holes, pores			bollita, pinchazos	40 ... 60 µm	in surface, locally or spread over product	Not visible with the naked eye, only by staining with colouring agents (methylene blue)
Small pinhole	Kleine Nadelstiche	kleine Nadelstiche	bollita, pinchazos	60 ... 80 µm	in surface, locally or spread over product	Visible with magnifying glass
Pinhole	Nadelstiche	Nadelstiche	bollita, pinchazos	80 ... 100 µm	in surface, locally or spread over product	Moiré-like, dusty surface aspect
specific: "iron"pinhole						contamination visible by magnifying glass op bottom of defect
specific: "body"pinhole						coloration visible on the bottom of the defect, into body
specific: "SiC " pinhole						contamination visible by magnifying glass op bottom of defect
Egg-skin	Eierschaligkeit		punto de aguja	80 ... 200 µm	in surface, evenly spread over product	egg-skin-surface: many small inward dented holes in surface
Orange peel	Orangenschale	sinaasappelhuid		200...400 µm	in surface, evenly spread over product	Scars from exploded bubbles, with sharp edges, not smoothed by firing
Bubbles in glaze	Blasen	Bellen	burbuja	200...400 µm	in surface, locally or spread over product	Holes from exploded bubbles, with smoothened edges
Soecific "SiC" bubbles						Holes from exploded bubbles, with smoothened edges, foaming is possible
Blisters, "Spit out"	Krätze		burbuja	> 400 µm	in surface, locally or spread over product	Scars from exploded bubbles, with sharp edges, not smoothed by firing.Sometimes coloration of surface (oil residues) Microscopic evaluation: cristaobalite residue and microfissures
	Krätze		burbuja	> 400 µm	in surface, locally or spread over product	Raw surface (even foaming is possible)
Crowfeet		kraaiepoten		> 500 µm	Cracks in surface, collapsed bubbles under surface, not smoothed	crowfeet, triangular cracks (branched)
Cracks				> 500 µm	Singular cracks in surface	Visible cracks
Big holes, open spots			poro, retiro	> 1000 µm	in surface, locally or spread over product	Open "spots", "retracted glaze"
"closed" surface defects (surface not disrupted)						
Bubbles under glaze	Blasenhaltige glasur	"mat"	burbuja	100 ... 200 µm	in surface, evenly spread over product, tipical location on kilncar	Matt aspect, small dents in surface (bubbles, not broken through surface but smoothened to closure, evt accompanied by small pinholes, or eggskin
Bubbles in glaze	Blasenhaltige glasur		burbuja	200 ... 500 µm		Dents in surface, bulging of glaze
"Quartz/cristoballite" pox	Stippen, Blebs	pokken		> 400 µm	in surface, locally or spread over product	precursor for spit out: comparable to pox, distinctive cristoballite/quartz relict
Pox	Pokken	pokken		> 400 µm	Bulges on surface, different sizes	pox in surface, pinlike protrusions from surface
Bulges under glaze	dellen	deuken		1 - 20 mm	big bulges, dents on surface, different sizes	Dents in surface, bulging of glaze

Figure 1. Excerpt of the classification matrix.

In figure 2 an example of the possible classification of the defects is given.

In the relation matrix, parameters of influence have been determined to identify appropriate remedies. This approach clarifies the distinction between direct "first degree" causes (direct defect generation, air inclusion) and influences (possible defect generation in combination with other setting or influencing parameters, early closure of the glaze combined with a degasification of a body- or a glaze component). This distinction has been added to the often used classification in primary causes (inclusions in the glaze matrix, e.g. by air inclusion in the glaze or deairation of the body) and secondary causes (changes and reactions in the glaze matrix, e.g. degasifications, changes in solubility of gaseous components). Different influences on a cause can be used to validate the appropriate action, keeping in mind its possible consequences.

Pinholes, 80 – 100 μm, in surface, locally or spread over product, underlying bubbles can be bigger than 100 μm, bubbles can occur over whole glaze layer

Pox, > 400 μm, bulges on surface, locally or spread over product, underlying bubbles are bigger than 100 μm

Figure 2: Classification examples

These aspects have been translated into a basic structure for the database, the "bubblebase". A software tool was chosen because providing database structuring and access through the interface in one step, web-enabled multi-user functionality and possible direct linking to common production control systems.

To incorporate the information 6 separate, but linked databases have been developed:

- Problems database (defects, topical general overview)
- Sources database (causes, topical overview)
- Remedies database (process control actions)
- Photos database (pictures, photos, trouble shoot reports, PDF)
- References database (literature (URL))
- Terminology database

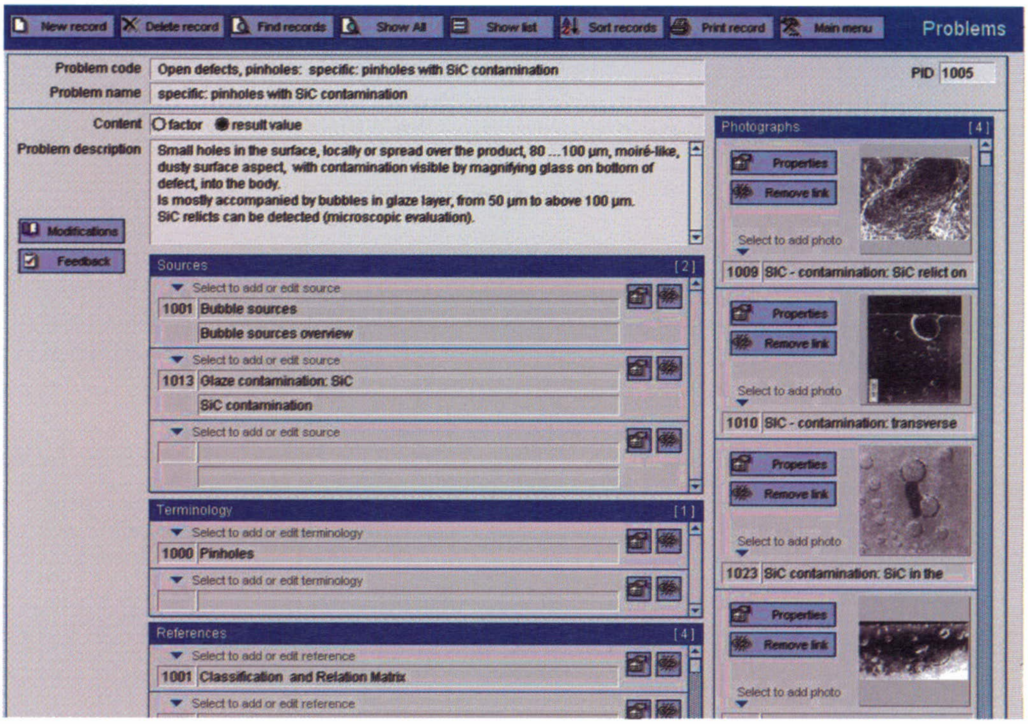
In this way, data and information can be easily added (including company specific knowledge like documents, reports, photographs), stored, linked or kept for future linking, and updated. The database can so be used to track defects to causes and define remedies, check influencing parameters, browse through the information in all databases and search on topics and terms, coming from different starting points. The database highlights the possibilities of a practical use of supporting software in the traditional ceramic industry. In figure 3 a screen print of the defect database can be seen.

3. PHYSICAL/CHEMICAL CHARACTERISATION OF MATERIALS AND PROCESSES

The glazes and bodies under consideration have been characterised using:

- Chemical Analysis by RFA/ICP
- Particle size distribution by laser diffraction (Malvern)

- Thermo analysis and gas desorption analysis by Simultaneous Thermo gravimetric Analysis (STA) combined with Fourier coupled Infrared Spectrometry
- Analysis of the melting behaviour by Hot Stage microscopy of the body and glaze and gradient firing tests
- Calculation of glaze parameters like viscosity and surface tension of glazes, using calculation techniques provided in the literature
- Analysis of bubbles amount and size distribution in production samples using microscopic image analysis, using a specially developed bubble count method
- Analysis of bubble content by Gas analysis by Mass Spectrometry



Problem code: Open defects, pinholes: specific: pinholes with SiC contamination

Problem name: specific: pinholes with SiC contamination

PID: 1005

Content: ○ factor ● result value

Problem description: Small holes in the surface, locally or spread over the product, 80 ...100 µm, moiré-like, dusty surface aspect, with contamination visible by magnifying glass on bottom of defect, into the body.
Is mostly accompanied by bubbles in glaze layer, from 50 µm to above 100 µm.
SiC relicts can be detected (microscopic evaluation).

Sources:
1001 Bubble sources — Bubble sources overview
1013 Glaze contamination: SiC — SiC contamination

Terminology:
1000 Pinholes

References:
1001 Classification and Relation Matrix

Photographs:
1008 SIC - contamination: SiC relict on
1010 SIC - contamination: transverse
1023 SiC contamination: SiC in the

Figure 3. Screen print from the defect database

The inventory of process parameters, their variation and the influence on bubble formation, have been evaluated based on these measurements. The influences of additives and impurities on the bubble generation have been taken into account. A classification of the materials has been made, to define representative system for further testing and model description. The classification has been based on:

- Raw glaze or glaze with fritted components
- Maximum working temperature below and above 1250 °C
- Tile, tableware and porcelain products

The use of the STA/FTIR analysis, providing information on the amount of degasification and the degassing components showed that for fritted glazes (lower temperature earthenware applications) there can be a degasification of H_2O above 1000 °C. Although the weight decrease is low (< 0.2 %) this is a considerable volume of gas. The origin of this effect is has not been investigated; a possibility is a thermostable hydration of the frit, decomposing at these temperatures.

In the characterisation, emphasis is put on parameters, which very directly indicate the glaze behaviour regarding bubble generation and bubble growth. In this regard the evaluation of the Hot Stage measurements, the gradient firing and the calculation of the viscosity of the glaze, based on these data, will be highlighted.

Image analysis of the video capture of the Hot Stage measurements of the glazes analysed by determining the two-dimensional change in height or surface area of the sample. This measurement is used to detect the starting point and the end point of sintering. Furthermore the two dimensional change in contact base line of the carrier and the glaze is measured, to define the point of minimal contact line. The contact angle of the sample on the carrier is measured. According the information from the literature evaluation, the following characteristic points for the melting behaviour were determined (Scholze[1]):

- SP = Sintering point: start of sintering, significant decrease of height
- MP = Minimal base line contact length, minimum wetting of the carrier material
- HKP = Half sphere point: height = 1/2 base line length, contact angle approx. 90°

According to Scholze[1] these points have a defined viscosity value, determined by empirical testing:

- SP = $\log \eta = 10.0 \pm 0.3$
- MP = $\log \eta = 6.0 \pm 0.2$
- HKP = $\log \eta = 4.55 \pm 0.1$

These three fix points have been used to solve the Vogler-Fuchler-Tammann equation to determine the dependence of the viscosity on the temperature for the glazes used in the project:

$$\log\eta = A + \frac{B}{T - T_0} \qquad [1]$$

The constants A, B and T_0 can be determined. In figure 4 the determination of the fix points from the graphs is illustrated.

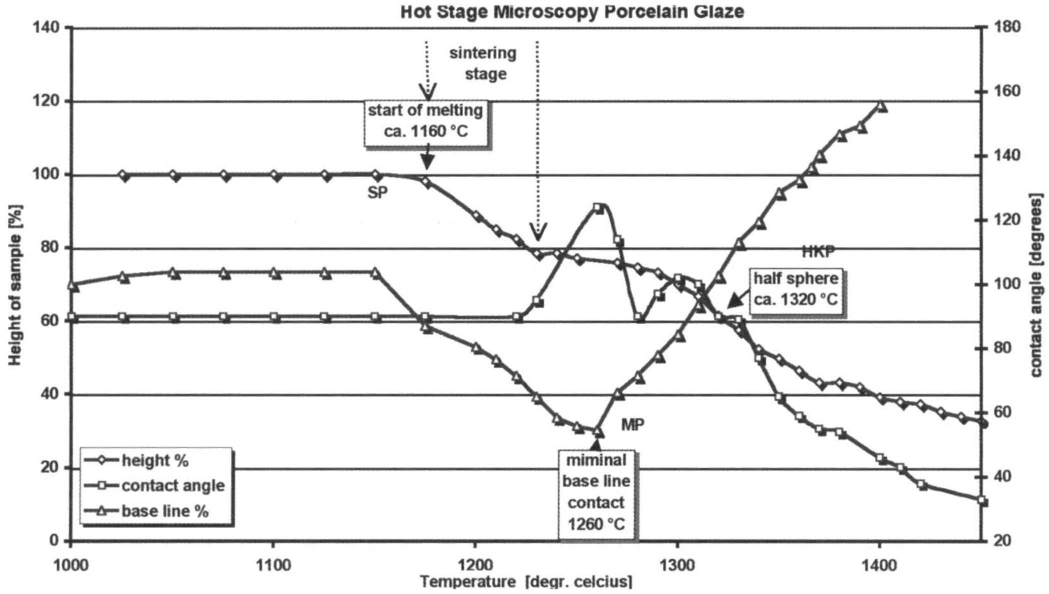


Figure 4: The determination of characteristic points from the Hot Stage graph evaluation

In figure 5 the resulting viscosity calculation is represented as a graph, underlining the differences between the specific glazes. These results have been used for further definition of the possible process control actions and have been used to validate the bubble growth model. In the graph the differences between tableware glazes, tile glazes for once firing and porcelain glazes can be seen. The tableware glazes require a lower viscosity at lower temperatures to ensure enough maturing of the glaze at low temperatures. The once firing tile glazes (with ZrO_2) require a large viscosity decrease in a short temperature interval, whereby the viscosity at maximum temperature should be low enough to ensure maturing of the glaze in the very fast once-firing cycle. This short temperature interval is needed because of the raw body reactions in the once firing process, which must have enough time to degas before closing of the glaze. The ZrO_2 component of the white tile glaze leads to the required high viscosity during the sintering/melting interval. The strong decrease with temperature means that the risk of overfiring (lower viscosity leading to escape of enclosed bubbles, leading to defects) has to be taken into account. The porcelain glazes are intended for higher temperature ranges and have a higher viscosity.

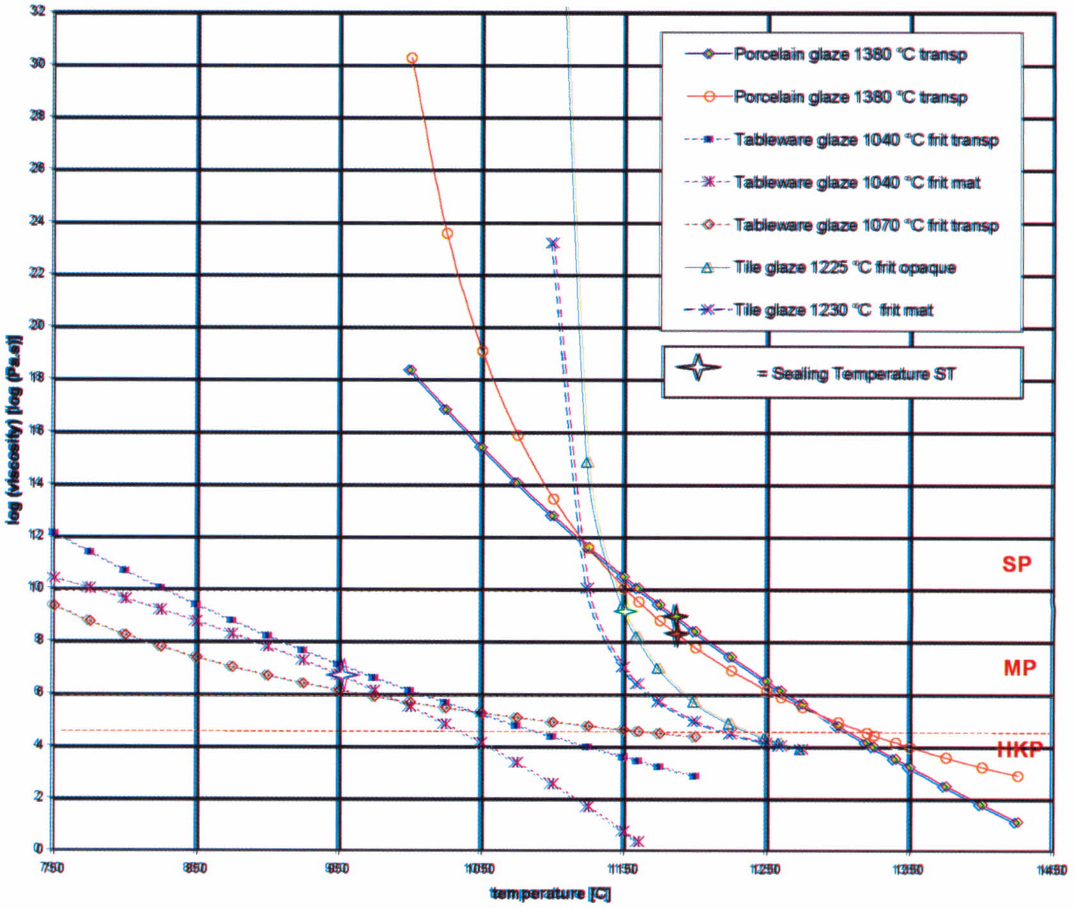


Figure 5: Viscosity graph based on the VTF-calculation using Hot Stage characteristic points for the glazes used in the project

An important aspect of the melting behaviour is the actual sealing of the glaze surface, which encloses the residual intergranular space to form bubbles. The viscosity at this specific point, as well as the viscosity development after this point determines the final bubble volume and bubble size distribution.

The sealing temperature can be estimated from the Hot Stage evaluation and compared, when using comparable glaze systems (Mestre e.a.[2]). In this case a practical approach was chosen by determining the sealing temperature (ST) by gradient firing and subsequent testing of the gradient sample by the ink test. In this test the transition from open to closed glaze surface is determined by looking at the changes in removability of ink applied on the surface of the sample. These differences in viscosity and sealing temperature imply the need to separately define specific process parameters and process control actions for the tableware, tile and porcelain production.

For evaluation of bubble patterns in the production samples the bubble count method developed by FGK was used using optical microscopy, coupled with a DCC camera, to define two dimensional bubble distribution and corresponding surface % bubbles. This evaluation of the glazes under consideration led to the following conclusions:

The bubble surface content in the porcelain glazes is about 8 – 10 % for a glaze thickness range of 170 – 250 μm, with an average bubble diameter between 30 – 50 μm. Average sizes and location of bubbles can differ due to composition, viscosity effects, kiln pressure and surface forces. These differences will be discussed later, using the bubble growth model description. The tile samples have a glaze thickness from 170-220 μm with a surface bubble % 9-12 %. The average diameter of the cross section of the bubbles is about 10 – 30 μm. The bubbles are equally distributed over the thickness of the glaze. Corresponding defects are eggshell/pinholes.

The transparent tableware glaze samples have a bubble surface amount of about 3%, located near the interface with the body with a maximum bubble diameter of 70 μm, while thicker transparent glazes have a bubble surface amount of 11%, with large bubbles up to 130 μm located near the interface with the body. The effect of the low viscosity enhancing as well bubble formation as bubble escaping can be seen. Colouring additions to the glaze, which lower viscosity, lead to less and smaller bubbles. The curing effect of the addition might explain this result. The table ware mat glazes have very large bubbles up to 130 μm located near the interface with the body, with (for the thicker glaze) bubble surface amounts of up to 46 %. The corresponding defect in the mat glaze is "pox" after decoration firing, probably due to growth of the large amount of bubbles.

To examine the bubble development as a function of glaze and temperature, later used also to validate the bubble model, gradient firing was used on prepared samples of body with production glaze, eventually glazed in production, after which the samples were evaluated using the bubble count method (figure 6).

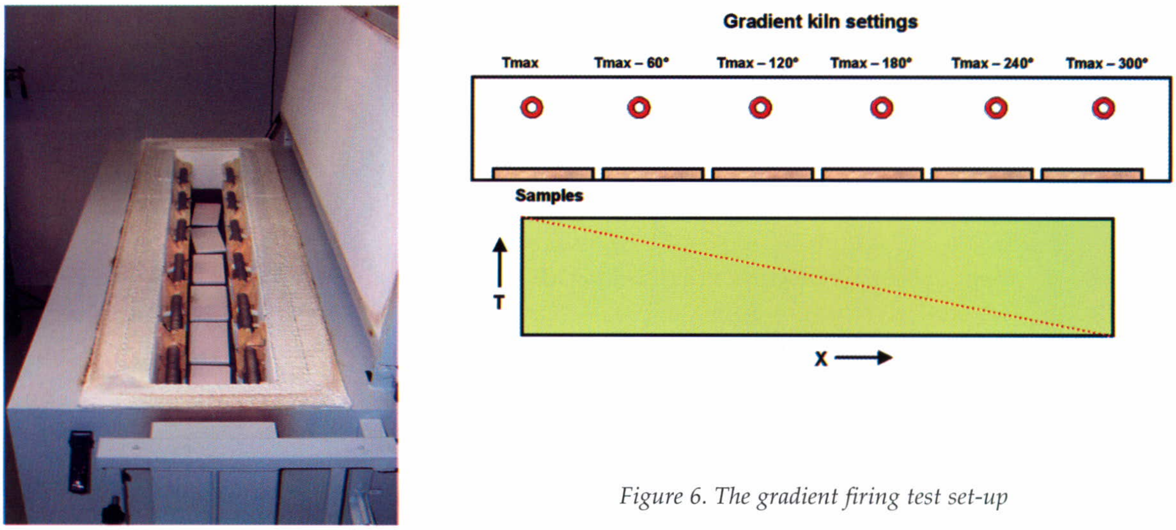
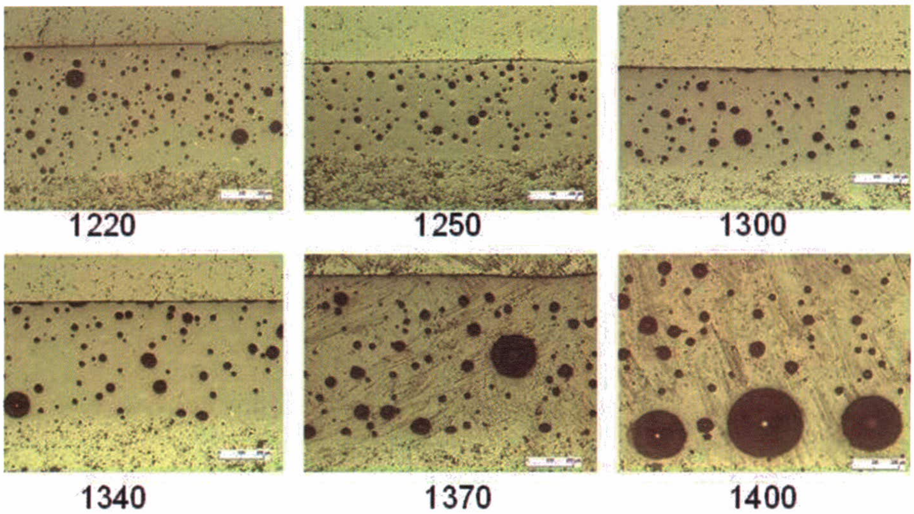


Figure 6. The gradient firing test set-up

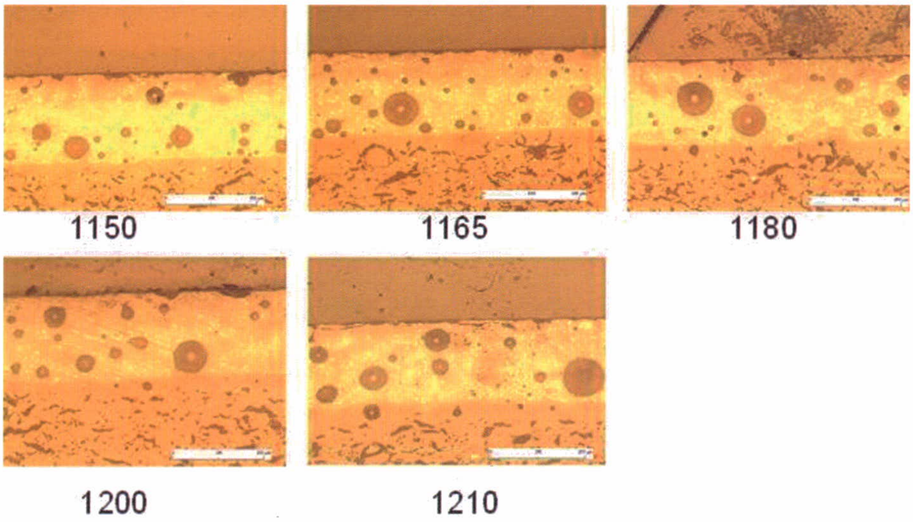
A typical behaviour of the porcelain glaze is shown in picture 7: the glaze has many small pores (10-30 μm) up to the working temperature of 1370°C. From 1370 to 1400°C the bubble surface content increases rapidly up to 20% at the glaze-body interface, with some very large bubbles, indicating overfiring to be a possible problem cause. This confirms the influence of changing solubility characteristics of different glaze components and the lower viscosity at higher temperatures on the porcelain glazes.


1220 1250 1300

1340 1370 1400

Figure 7: Bubble development in a porcelain glaze during gradient firing to 1400°C

A typical behaviour for once- firing tile glazes can be seen in figure 8. The glaze has a bubble content up to 10%, with bigger bubbles (70 – 80 μm) developing at higher temperature, with most of the bubbles in the glaze body interface. Here the influence of the large interaction between raw body and glaze can be seen: due to a reactive, and therefore well-developed intermediate layer, this layer contains bubbles at higher temperatures, which at first sight seem to be in the body.


1150 1165 1180

1200 1210

Figure 8: Bubble development in a once-firing tile glaze during gradient firing to 1250°C

4. PHYSICAL/CHEMICAL DESCRIPTION OF BUBBLE GENERATION AND DEVELOPMENT

To develop a model describing the mentioned effects, the descriptions used in the glass area for bubble movement and growth has been translated to the glaze area. A quantitative model description for bubbles in glaze layers has been developed based on the mathematical model for the Ostwald ripening using bubble growth equations, bubble movement equations and the Stokes-Einstein equation for gas diffusion.

The following parameters have been taken into account:

- Surface tension
- Concentration
- Solubility
- Diffusion
- Viscosity
- Pressure
- Porosity at closure of the glaze

The relation between control actions in the factory and the bubble behaviour in the glaze has been made explicit using the model description. Based on differences in the relevant parameters like viscosity and working temperature a differentiation is made between glazes with a Tmax < 1250°C (tableware, tiles) and Tmax > 1250°C (porcelain). For the glazes used in the project gradient firing was used to validate the model description.

A computer simulation program was made using the basic equation for bubble growth:

$$dr/dt = K'/r \ (1/r_m - 1/r) \qquad [2]$$

In addition the movement due to gravity is taken into account:

$$dy/dt = 2/9 * r * 9.8 * r^2/h \qquad [3]$$

The input parameters are:

- The initial mean radius: r_m
- The rate constant K', taking into account solubility of the gaseous component, the concentration at the surface, partial pressure and the viscosity at the surface of the bubble.
- The volume percentage closed porosity: v
- The viscosity of the glaze h
- The density of the glaze r

It is supposed that the bubbles are randomly distributed in the layer. Further a random distribution of bubbles (up to 2 times r_m) is supposed as initial size distribution. Using these parameters the growth of the bubbles is simulated in time. The disappearance of the small bubbles can be followed as the growth of the large bubble. In addition it is visible that the large bubbles rise in the glaze layer.

Important conclusions, which can be drawn from the description and calculations using the mathematical model:

- Up to sealing temperature gasses can be removed, no bubbles are formed
- After sealing bubble diameters correspond with existing pressure and enclosed porosity
- If above the sealing temperature gas is released from the body, it will be incorporated in the glaze matrix
- Gas dissolved in glaze is released by:
    - Super saturation
    - Concentration/partial pressure differences
- On a ceramic substrate these effects can lead to bubble generation at higher temperatures (overfiring, T>Tmax)
- Due to solubility effects of gaseous components bubbles can be generated and grow due to changes in the glaze (increased acidity by glaze-body reactions)
- Large bubbles grow consuming small bubbles
- Large bubbles move due to gravity: upon reaching the surface defects can be generated due to bubble collapse
- If the bubble diameter exceeds the layer thickness, collapse can lead to bubble defects

The calculations using the model define a quantitative relationship between growth rate and diameter, and bubble size distribution and time (Figure 9): the smaller bubbles tend to disappear, while bigger bubbles grow. The mean bubble diameter grows with the inverse third power of the time.

These relations have been successfully validated using the bubble counts of the gradient tests.

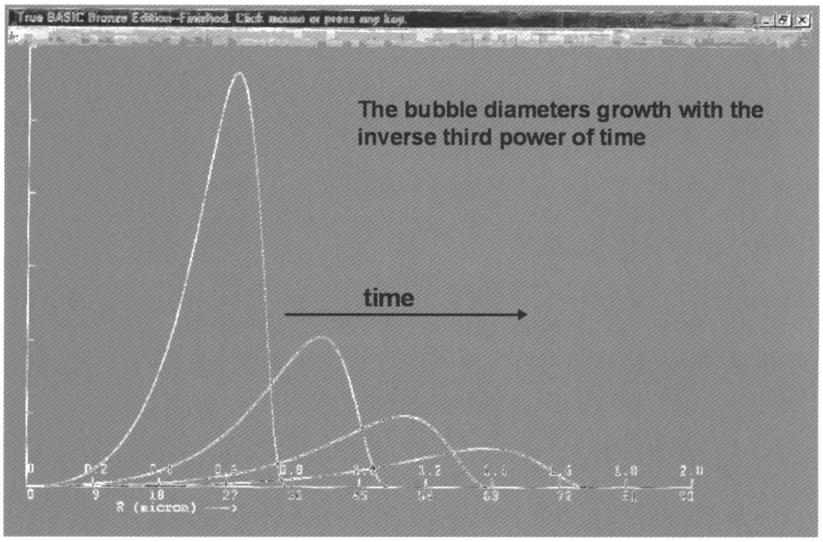


Figure 9. The change in the bubble size distribution in time based on the growth rate as derived fro the quantitative bubble model

The model was also validated using the measurements of the bubble content, which however have to be interpreted carefully, due to influences of rapid diffusion reactions: glaze samples are broken under vacuum, the gas is analysed on O_2, CO, CO_2, H_2O, Ar, N_2, C_xH_y, Cl_2, F, SO_2 and H_2 in an mass spectrometer. Some components dissolve very rapidly in the fresh fracture surfaces (H_2O). The results of the measurements indicate that in most of the bubbles mainly nitrogen and carbon dioxide is present. The nitrogen/argon ratio corresponds to the ratio in the air, supporting the idea of inclusion being the main cause for the presence of bubbles.

It is clear that only the gases, for which the glaze matrix has low permeability (N_2, CO_2), stay behind in the bubbles.

A new method, heating chamber microscopy, that recently became available, was incorporated because of its possibility for direct visual qualitative assessment of the effects as indicated by the model: a glaze sample of an diameter of 2 –3mm (droplet) is placed in a heating chamber, which can be heated up to 1500ºC. During the heating (which can be temperature and time controlled) the sample reactions can for the first time be seen real-time, using a microscope, and recorded on (digital) video. The measurements gave for the first time a possibility to see the glaze melting behaviour and confirmed the following effects, as derived from the model description:

- At sealing temperature inclusions lead to bubbles, no new bubbles are formed.
- Bubbles of 100 μm and bigger move due to gravitational forces, the effect is more clear for the low viscosity glaze.
- Large bubbles of 100 μm and bigger can be seen to grow.
- Bubbles, which reach the surface, implode very quickly, the surface "heals". Also this effect is more pronounced for the low viscosity glaze.
- Bubbles, which come in contact, coalesce very quickly (in high as well as low viscosity!)
- New bubbles of ca. 10 μm are generated at higher temperatures; they " burst" into existence. This effect is clearer for the high viscosity porcelain glazes, due to solubility changes.
- The bigger bubbles can be seen to shrink during cooling.

5. DEVELOPMENT OF PROCESS CONDITIONS TO CONTROL BUBBLE FORMATION

The mathematical model for Ostwald ripening, based on the bubble growth equations and on the equation for Stokes-Einstein movement, can now be used to determine the influence of surface tension, concentration differences, solubility of gas components, diffusion, viscosity and pressure, as a function of the temperature.

It can be concluded that for low viscosity glazes bubble movement can lead to a fining effect, so viscosity effects and the firing cycle are very important (table ware glazes). In this case additives to fine the glaze are only of limited use. For high viscosity glazes initial bubble distribution is very important, the green density of the glaze is more important (tile and porcelain glazes). Reducing viscosity (enhancing bubble movement to the surface) by overfiring in this case can lead to a very defective surface. In this case fining agents (based on anionic fluxing behaviour) can be used to help the surface to "cure". In the case of degasification reactions a high sealing temperature and a high viscosity of the closed glaze at that stage are beneficial (tile glaze). Table 1 summarises the impact of processing parameters to be used to define the possible control actions in the production.

Influencing parameter	Tmax ≤1250 °C (medium viscosity at sealing temperature, tableware)	Tmax > 1250 °C (high viscosity at sealing temperature, tiles and porcelain)
• Firing cycle:		
○ Gradient	++	+
○ Tmax	+	++
• PSD Glaze	+	++
• Glaze Thickness	++	+
• Glaze application	+	++
• Additives for glaze	-	+
• Densification body	++	-
• Reactions body	++	-

Table 1. Impact of influencing parameters for different glaze types

The choice of parameters to be tested and validated for process control regarding bubble defects was defined for each of the participants, according to the table 1 and a scan of the process control possibilities on site. The results can be summarized as follows:

For the porcelain glazes (T > 1250 °C, high viscosity):

- Smaller grain sizes increase sensitivity to crawling, bigger grain sizes lead to irregular surfaces.
- Smaller grains lead to decrease in the melting temperatures and have a deteriorating effect on surface quality (enclosure at lower viscosity), leading to more, but smaller pores
- Grain size has only limited influence on the viscosity, but an important influence on reference temperatures in the melting behaviour (start melting, sealing, half sphere), without altering the melting intervals
- The bimodal character of a ceramic glaze particle size distribution (mineralogical components or frit mixtures) imply a minimal degree of milling to reduce the possibility of bubble defects by e.g. coarse quartz distributions leading to an increased viscosity in the glaze, or even local defects by large quartz relicts
- For porcelain glazes fining additions to the glaze lead to deterioration of the surface, due to lowering the viscosity to enhance bubble escape of big bubbles at a high viscosity level, with limited surface curing.
- Fining additions on the glaze lead to an improved surface quality, however very sensible to the application practice. A bubble-free layer of about 30 μm can be formed, sealing the top layer.

For tile glazes (T < 1250 °C, high viscosity):

- Adjusting the firing curve according to the degasification behaviour of body and glaze and the sealing temperature (which has to be known), avoiding overfiring, increases the surface quality
- The use of additions is comparable to the situation for porcelain glazes. In this case due to the strong viscosity decrease at the working temperature the

fining effect of the additive should be less. The choice of additives with limited fluxing behaviour confirmed this.

For tableware glazes (T < 1250 °C, low viscosity):

- The combination of degasification reactions and the firing curve are also important, in regard to the situation for tiles; however, the glaze can be fined by higher temperature due to the low viscosity.
- In this case the glaze thickness plays an important role, due to the mobility of the bubbles at higher temperature

Based upon these differences in approach for the different glaze systems the new tools, being the database as well as the glaze characterisation methods can be used to create an overall routine for bubble control for ceramic glazes, as given in figure 10.

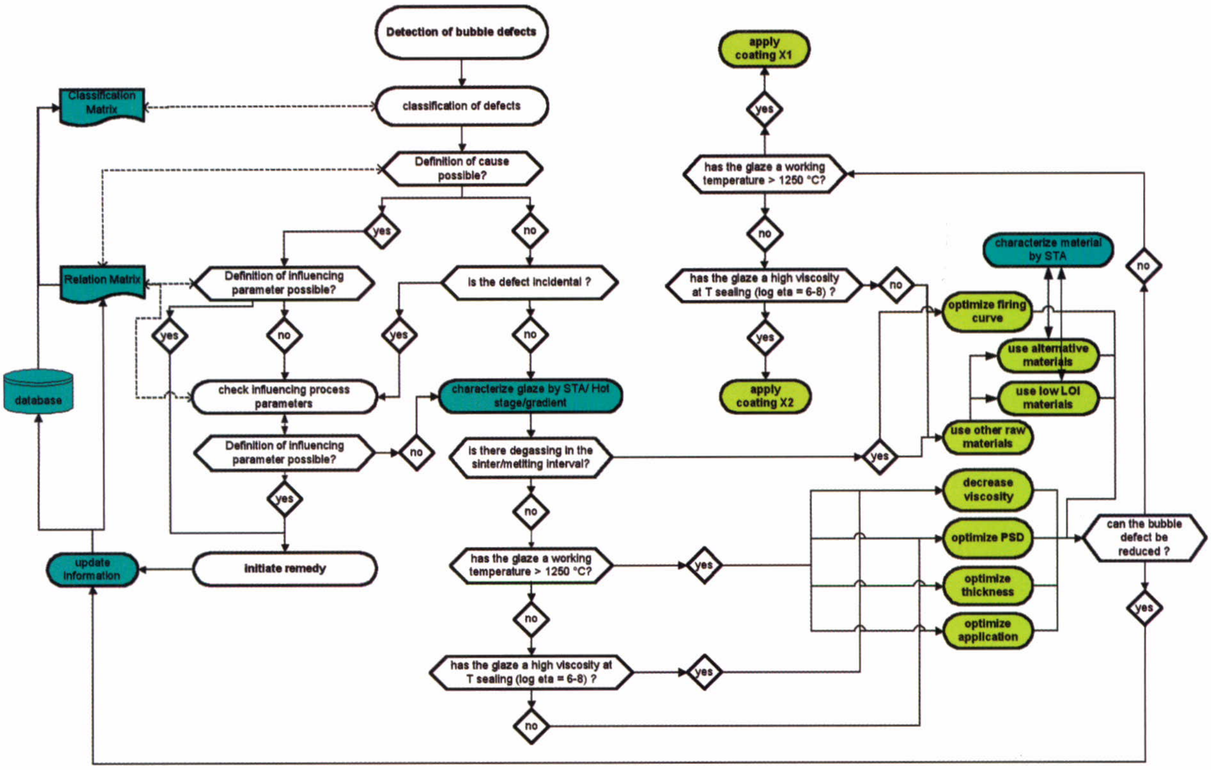


Figure 10. Decision diagram (bubble control routine) to define the possible control actions regarding bubble and pinhole control for ceramic glazes

6. PERFORMANCE OF PRE-PILOT AND PILOT TESTS

Based on the definition of relevant parameters to be tested and the results of the first laboratory scale experiments, production tests have been performed to simulate conditions to control bubble generation during factory production processes. As illustrated in the bubble control routine (figure 10) for each of the participants the possible control actions have been determined and quantified according to the table 2.

Glaze	Process conditions	Targets	Description of control actions
Porcelain	Firing curve	Optimised Tmax, degassing, burner setting	Adjusted Tmax, gradient
	Grain size distribution	Controlled PSD	Adjusted ball milling or glaze specs
	Thickness of glaze	Optimal thickness	Adjusted spraying and dipping
	Application of glaze	Optimal density	Viscosity-density adjustments
	Additives	Coating	Coating by spraying in production
	Body densification	Optimal pressure	Densification adjustment
Tile	Firing curve	Optimised Tmax, degassing	Adjusted Tmax, gradient
	Additives	Coating	Coating by spraying in production
Tableware	Firing curve	Optimal gradient, degassing	Adjusted Tmax , optimised gradient
	Grain size distribution	Improved milling efficiency	Adjusted ball milling Adjusted glaze composition
	Thickness of glaze	Optimal thickness	Application technique
	Application of glaze	Optimal application	Application technique
	Reactions of the glaze	Optimal temperature Optimal composition	Optimal curve Controlled frit quality
	Reactions of the body	Optimal conditioning	Optimal storage

Table 2. Specification of pre-pilot and pilot tests

7. CONCLUSION

The implementation of the improvement possibilities as defined has achieved a reduction of the bubble defects for the participants of at least 10 – 50 %. The achieved reduction consists of surface improvement, reject reduction, and calamity prevention. The actual reduction depends on the specific production situation. The risk reduction regarding bubble defect calamities has been estimated based upon the experience of the last years during the ceramic production processes. The quantification of these results also takes into account the productivity improvement potential, defined and planned for implementation, leading to considerable revenue potential. These results have been defined in detail for each participant.

The embedding of the developed knowledge to support the development of glazes with innovative functional aspects will be one of the topics fur further research in follow-up projects, as defined by the response of the market to the published and presented results.

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REFERENCES

[1] H. SCHOLZE, „Der Einfluss von Viskosität und Oberflächenspannung auf erhitzungsmikroskopische Messungen an Gläsern", Ber. DKG 39 (1962) no. 1, 63-68,

[2] S. MESTRE, E. BOU, P. QUEREDA, A. BARBA, "Using the Hot Stage Microscope for estimating Frit Sealing Temperature", cfi / Ber. DKG 78 (2001), No. 9.

In the mentioned inventory a large number of references were collected and evaluated. For an overview of the references please refer to the authors.