Experimental Study of the Effects of Clay Washing on the Reduction of Glaze Pinholes

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Ceramic raw materials impurities such as sulfate, organic substances, and other soluble salts may generate gaseous bubbles during the firing process at high temperatures that expand in the glaze and burst, leaving pinholes on the surfaces. This paper aims to understand the correlation between the glaze pinhole severity and the soluble salts level in the used clays in the sanitaryware body. Samples were highlighted in this study to track the soluble salts, especially the sulfate content before and after washing. Washed and unwashed samples were tested using the X-ray fluorescence chemical analysis and Dionex chromatography to measure the sulfate anions of the clays, followed by a naked eye test on the fired sample confirmed by the optical results obtained by laser speckle technique. The results of the washed samples show significant improvement in decreasing glaze pinholes confirmed by the laser speckle technique and aligned with low sulfate content measured and proved by the Dionex cromatography compared to the samples prepared by the same clays before being washed.

1 Introduction

Glaze pinholing is a common and problematic phenomenon in the sanitaryware industry that has a detrimental effect on the industry's production cost and quality performance. The factors which have an influence in causing the formation of glaze pinholes extend from the raw materials selection to the firing cycle, including most of the processing parameters and these factors have been identified by several researchers [1–6]. Once the existing causes are defined precisely, the intensity of the glaze pinholing can be altered by controlling or eliminating those factors/causes. From a perspective point of view, the glaze pinhole is a gas bubble formed during the production stages of ceramic pieces that burst on the glaze surface and are not released as the glaze solidifies [4]. Sources of gassy bubbles can be divided into three main categories [2]:

1 Gases released by glaze and body components decomposition during firing
2 Formation of bubbles in body porosity and glaze processing
3 Gas released by contaminated raw materials such as soluble salts.

The most critical time for the decomposition of impurities is once the gassy bubbles are formed in conjunction with the glaze solidification temperature that is taking place [1]. As stated, some of the gases responsible for the defect are CO_2, SO_3 and SO_2 which have been proved by many experiments and studies in the literature as a result of certain salts decomposition, which have been proved [1]. This study highlighted the impact of the clay contamination on the sanitaryware articles, especially sulfate, knowing that several factors affect the intensity of the glaze pinhole, such as sulfates that exist as impurities in the raw materials, water used in production and also the abrasion of plaster moulds in the return slip. The sulfates of alkali or alkaline-earth metal and/or sulphides (pyrite FeS_2 or chalcopyrite $CuFeS_2$) present as impurities in sanitaryware ball clays and/or China clays decom-

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pose and release SO_3 and SO_2 [1, 7, 8], according to the following chemical reactions:

$S + O_2 \rightarrow SO_2 \uparrow$
at about 250 –920 °C

$FeS_2 + O_2 \rightarrow FeS + SO_2 \uparrow$
at about 350–400 °C

$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2 \uparrow$
at about 500–800 °C

$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3 \uparrow$
at about 560–775 °C

$CaSO_4 \rightarrow CaO + SO_3 \uparrow$
above 1180 °C

$BaSO_4 \rightarrow BaO + SO_3 \uparrow$
above 1000 °C

In slip preparation, barium carbonate has been used as a precipitating agent of the soluble sulfate [9]. The following reaction shows an example of how the soluble sulfate interacts with barium carbonate.

$$BaCO_3 + Ca^{2+} + SO_4^{2-} \rightarrow BaSO_4 + CaCO_3$$

The precipitation of barium sulfate helps in improving slip characteristics however, according to Mahin and Kilian and previous investigations, the behavior of barium sulfate at high temperatures differs according to the existence of silica and ferric oxides also may present a negative effect during the glaze solidification [8]. The pure barium sulfate decomposes near 1500 °C, but in this case, the body composition contains a high percentage of silica which decrease the decomposition temperature of the latter to be around 1000 °C which is below the usual maximum temperature in sanitaryware. Based on the literature, sulfate and other soluble salts present in the clay used in the production of sanitaryware body can be decreased by ordinary clay washing [9].

During clay firing, the carbon is transformed into carbon dioxide and carbon monoxide gases in the presence of oxygen. The reaction temperature starts from 600 °C and varies depending on some factors like the kiln cycle length and temperatures, the shape and quantity of carbon contamination, the kiln atmosphere (oxidation), and the piece shape configuration. If the reaction does not complete below 760 °C, it causes incomplete degassing problems like glaze pinhole [2]:

$C + O_2 \rightarrow CO_2 \uparrow$
common range from 600–760 °C

The quartz transition temperature is 573 °C, the decomposing temperature of organic matter is 400–600 °C, carbonates decomposing temperature is 700–1050 °C and sulfates decomposing temperature is 950–1100 °C. Some of these transformations lead to degassing and formation of defects, such as pinholes or detachment of glaze from support [10]. Based on the literature of previous research, there appears to be enough information to hypothesis that high levels of sulfate content can increase the glaze pinholing. This study will evaluate and confirm the correlation between the glaze pinhole severity and the soluble salts level in the used clays by implementing a specific washing procedure. The obtained results will be subject to the laser speckle technique to validate them and be able to industrialize this study by any sanitaryware manufacturer.

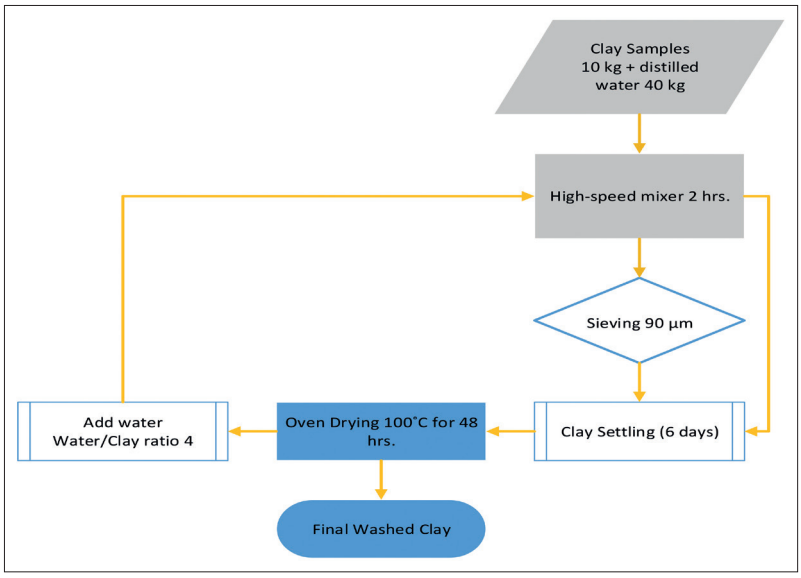

Fig. 1 Illustration of the washing process

2 Experimental

The raw clay washing procedures outlined by Mahin and Bro Kilian have been modified so sulfate ions were properly removed [11]. The batches of English ball clay V8 (mass-%: SiO_2 56,7 %, Al_2O_3 27,4 %, TiO_2 1,3 %, Fe_2O_3 1,1 %, CaO 0,1 %, MgO 0,3 %, K_2O 2 %, Na_2O 0,3 %; 10,4 % L.o.I., and carbon 2 mass%) and China clay remblend (mass-%: SiO_2 48 %, Al_2O_3 36,5 %,TiO_2 0,05 %, CaO 0,07 %, MgO 0,3 %, Na_2O 0,10 %; and 12 % L.o.I.) were first washed in the laboratory by stirring 10 kg of dry material with 40 kg of distilled water (water-clay ratio 4) for 2 h using a high-intensity mixer before pouring through a 90 µm sieve. The mixture of distilled water and clay was then passed over magnetic rods. The clay suspensions were kept for 6 days until the clay settled. The upper layer of water was removed, and the wet settled clay was dried in the oven at 100 °C for 48 h. The dried clays were again dispersed in distilled water (water-clay ratio 4) and stirred for 2 h. The clay suspensions were kept for 96 h until the clay settled, and the previous washing procedures were repeated again.

An impractical number of washings would be needed to remove all sulfate ions. Therefore, the ASTM C867-94 (2014) Standard Test Method for Soluble Sulfate in Ceramic Whiteware Clays was considered to evaluate the efficiency of the laboratory washing procedures [12]. Samples of clay water before and after washing were prepared according to the test method procedures to determine the amount of soluble sulfate ions present [12]. The sulfate content in water was measured using the HI 93751 meter. Sulfate was precipitated with help of barium chloride crystals. Light absorbance

of the suspension was measured. The light source was emitting diode at 470 nm and light detector was a silicon photocell. The reagents are powder and were supplied in packets with the instrument. The amount of reagent was precisely dosed to ensure maximum repeatability. This test method should be considered only as a control test and not a quantitative analysis for sulfate ions as stated in the standard [12].

Further samples of laboratory washed clays and normal unwashed clays were quantitatively analyzed using X-ray fluorescence (Bruker/DE, S4 Explorer) used to determine the elemental composition of clay materials and the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. The Dionex chromatography (Thermo Scientific ICS2000) was used to measure the actual sulfate content in clay samples in external laboratories of IMERYS/GB and SIBELCO/GB. The process illustration is shown in Fig. 1.

Slip samples (slip 1 and slip 2) were prepared in the laboratory with the same body compositions for vitreous china from the washed (final-washed clay) and unwashed clays, both sieved at 90 µm, in order to evaluate the impact of decreasing clay sulfate such as Iron sulfates, calcium sulfates, barium sulfates etc. which degases SO_2 and SO_3 leading to the glaze pinhole.

The samples were cast in form of a square tile (10 cm x 10 cm x 1 cm), and glazed on both sides using the same glaze of a vitreous clay composition prepared by Lecico Egypt, as in normal production to ensure repeatability [13]. All samples were horizontally fired in the same tunnel kiln within the normal production. The firing conditions were: firing cycle time 16 h, soaking temperature 1197–1205 °C, and soaking cycle time 58 min (Fig. 2).

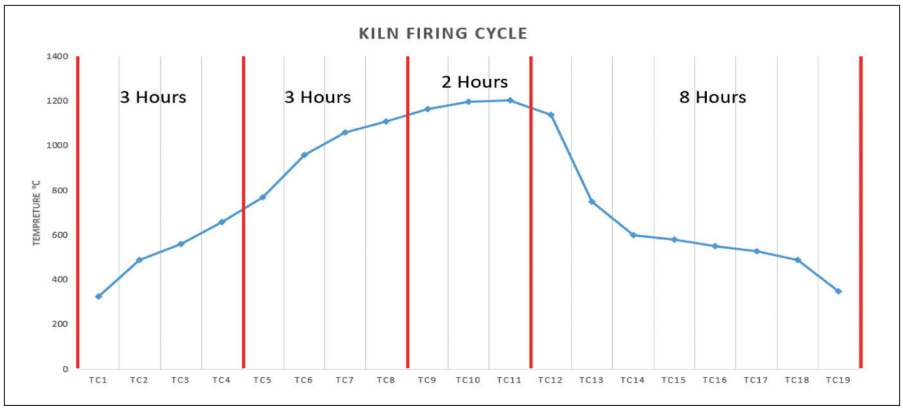

Fig. 2 Firing Cycle

The glaze pinhole was measured using an index of pinhole density [no./cm^2] [13]. The surface of fired tile samples was also analyzed using the laser speckle method [14–16]. A speckle phenomenon occurs whenever spatially coherent light is reflected by a rough surface or propagates through a random medium. A 15 mW and linearly polarized He–Ne laser with a wavelength of 632,8 nm and an optical coherence length of 20 cm was used to illuminate the tiles as shown in Fig. 3a. The laser beam diameter was extended using a beam expander in order to cover the largest surface of the tile and hence the largest number of pinholes. The parallel component of backscattered light from the surface of each of the samples was collected by a Complementary Metal Oxide Semiconductor CMOS camera (MotionBLITZ EoSens mini1, pixel size 14 µm × 14 µm), providing the speckle image (Fig. 3b). Two speckle parameters were extracted from each set of the acquired images. The first one was the speckle grain size which is the width at half maximum of a horizontal section of the normalized auto-covariance function of the speckle intensity [15].

One can also estimate the speckle grain size dx using the Li and Chiang equation:

$$dx = \frac{1{,}22\,\lambda\,D}{D_e cos\theta}$$

where D, λ, D_e and θ are the distance between the sample and the camera, the wavelength of the laser, the diameter of the scattering spot, and the angle between the incident beam and the one detected by the camera, respectively [16]. In these experiments, D was set to 20 cm and θ = 20°, in order to avoid direct beam detection. The second one is the contrast of the speckle image defined as the ratio between the

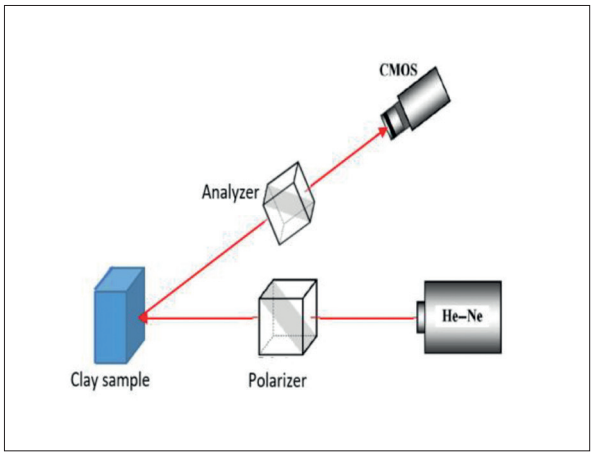

Fig. 3a Overview of the speckle experimental setup

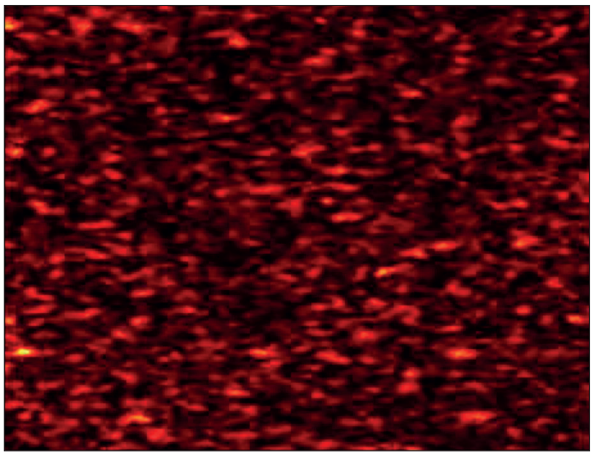

Fig. 3b Example of a speckle image

Tab. 1 Sulfate analysis (sulfate content in the clays water and clay sulfate anions determined by means of Dionex chromatography)

	Water Sulfate Content by HI 93751 [mg/l]	SO_4^{2-} Content by Dionex Chromatography [ppm] Std. Dev. 1/15 ppm
Ball clay (before washing)	120	244,5
Ball clay (after washing)	93	209,0
China clay (before washing)	80	221,0
China clay (after washing)	25	56,0

intensity standard deviation and the mean intensity of the speckle pattern [17].

3 Results and discussion

3.1 Chemical analysis

Sulfate content in the clays water: The sulfate content in the clays water according to ASTM C867-94 (2014) was determined using the in laboratory. The reduction in China clay after washing was 68,75 %, and in ball clay it was 22,50 % (Tab. 1).

Sulfate anion analysis: The quantitative analysis results (Dionex chromatography) for sulfate ions after washing showed a huge reduction in the soluble sulfate content in the China clay i.e. 74,66 %. The washing process also showed a significant reduction in the actual soluble sulfate content within the ball clay i.e. 14,52 % (Tab. 1).

XRF analysis: The XRF chemical analysis techniques were used to track or highlight any significant changes in the used clay chemical analysis as shown in Tab. 2 for China clay and for ball clay after washing.

Pinhole index: On the other hand, the qualitative analysis using the total pinhole index of the fired samples after clay washing showed a high improvement of 81,82 % (Tab. 3).

The results of the HI 93751 sulfate meter (Tab. 1) showed that the total soluble sulfate decreased in the clays water after washing in laboratory by a significant percentage, this giving the indication that washing was efficient and had an impact on the decrease of the sulfate amount in the clays. After firing, the glazed surface of the sample tiles was visually reviewed looking for the presence/severity of glaze pinholes. To the naked eye, the amount of glaze pinholes appeared to have significantly improved on the tiles produced from clays that were washed compared to the tiles produced from unwashed clays (Fig. 4a–b).

Tab. 2 XRF analysis

	SiO_2 [mass-%]	TiO_2 [mass-%]	Al_2O_3 [mass-%]	Fe_2O_3 [mass-%]	CaO [mass-%]	MgO [mass-%]	K_2O [mass-%]	Na_2O [mass-%]	L.o.I. [%]
BALL CLAY V8									
SIBELCO Laboratory									
SD	0,20	0,03	0,20	0,03	0,03	0,02	0,03	0,20	0,00
Before washing	56,30	1,27	27,00	0,98	0,11	0,31	1,95	0,28	11,23
After washing	56,00	1,28	27,50	0,98	0,13	0,32	1,95	0,26	11,04
IMERYS Laboratory									
SD	0,13	0,00	0,10	0,00	0,00	0,00	0,00	0,00	0,00
Before washing	57,20	1,31	27,60	1,03	0,13	0,2	1,97	0,22	10,30
After washing	56,60	1,33	28,00	1,03	0,14	0,21	1,92	0,18	10,40
Average									
Before washing	56,75	1,29	27,30	1,01	0,12	0,26	1,96	0,25	10,77
After washing	56,30	1,31	27,75	1,01	0,14	0,27	1,94	0,22	10,72
KAOLINS Remblend									
SIBELCO Laboratory									
SD	0,20	0,03	0,20	0,03	0,03	0,02	0,03	0,20	0,00
Before washing	47,90	0,07	36,10	1,08	0,04	0,27	2,19	0,08	11,90
After washing	48,10	0,06	35,80	1,12	0,05	0,27	2,24	0,10	11,76
IMERYS Laboratory									
SD	0,13	0,00	0,10	0,00	0,00	0,00	0,00	0,00	0,00
Before washing	49,10	0,11	36,20	1,12	0,05	0,19	2,3	0,03	11,2
After washing	48,30	0,07	36,80	1,16	0,06	0,19	2,26	0,00	11,4
Average									
Before washing	48,50	0,09	36,15	1,10	0,05	0,23	2,25	0,06	11,55
After washing	48,20	0,07	36,30	1,14	0,06	0,23	2,25	0,05	11,58

Tab. 3 Pinholes index

Sample	Index of Pinhole Density [nr./cm²] SD 0,02
Slip 1 (Clays before washing)	0,33
Slip 2 (Clays after washing)	0,06

Tab. 4 Speckle image contrast results

Sample	Speckle Image Contrast
Slip 1 (Clays before washing) 0,33 [nr./cm²]	0,495 ± 0,003
Slip 2 (Clays after washing) 0,06 [nr./cm²]	0,484 ± 0,006

The results from the trial tiles confirmed that the clay washing technique does indeed decrease the clays soluble sulfate as stated by H. R. Shell and B. P. Cortelyou and by decreasing the sulfate content in the body raw materials, the effect was also positive on the intensity of the development of pinholes in the glaze [9]. This was further supported by the results shown in the sulfate analysis: the results clearly showed that the actual existing content of sulfate decreased in both ball and China clays.

3.2 Laser speckle analysis

For the optical analysis of the tiles' surface using the laser speckle method, the diameter of the laser scattering spot on the samples did not show any notable variation between samples. This observation was confirmed by the results of the speckle grain size (average value = 7,1 ± 0,1 pixels) which did not present any significant deviation from one sample to another. This is probably because the main structure of the China and ball clays didn't change before and after being washed [17]. As shown in Tab. 4, the contrast of the speckle image decreases after washing. In fact, a relative variation of 2,3 % in the contrast results was measured in the case of tiles before and after washing which prove a large effect on the pinhole density.

As a matter of fact, the clay surface is a non-absorbing surface and it backscatters largely incident light. Hence, the detected signal can be used as an indicator to assess the quality of the tiles' surface. Before any washing process, the tiles present many scattering events on their surface, indicating that the surface scattering contribution overcomes the volume scattering contribution [18]. These results in relatively large contrast values. After washing, the pinhole density decreases and the surface of the plate presents less non-homogeneities in terms of pinholes. Hence, a predominant volume backscattering occurs, yielding a decrease in the speckle contrast values as illustrated in Fig. 6. When plotting the optical results of the two samples as a function of the index of pinhole density, the results showed that the speckle image contrast decreased as the pinhole density decreased.

4 Conclusions

Several analytical techniques were used on the clays in order to study the soluble salts and the undesired impurities. Washing procedure was conducted and verified as a solution to reduce significantly the sulfate content in the clays based on the lower levels obtained. Visual pinhole results of the fired ceramic samples proved also a correlation between clays contamination such as sulfates and the pinhole density recorded: the less contamination of the used clay, the lower pinhole density obtained. The difference in speckle patterns revealed progress from surface to volume backscattering when the pinhole level decreased and the surface introduced less spatial varieties. Quantitative records of this work confirmed again that the selection of the used clays in the vitreous slip composition directly affected the glaze pinhole. A perspective to work on in the development of this topic is to find and identify other potential elements which could have a direct impact on the pinhole severity such as carbonates, coal, lignite, etc.

Acknowledgments

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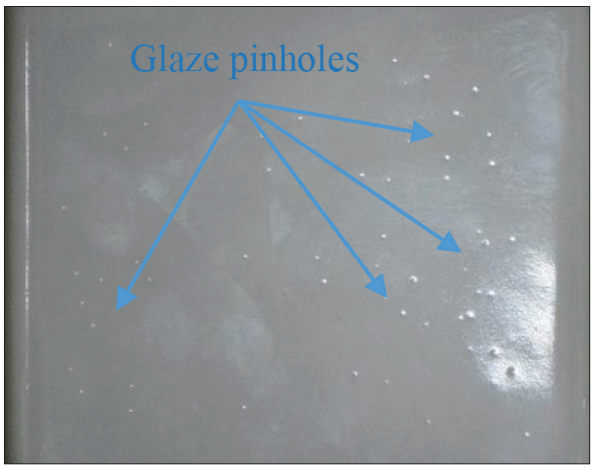

Fig. 4a Fired tile sample obtained with unwashed clay

Fig. 4b Fired tile sample obtained with washed clay

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