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Chemical hardening of glazed porcelain tiles

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Abstract: Glazed ceramic tiles are used for wall and floor covering thanks to theirs high resistance to chemicals attacks, although big efforts should be done to increase their surfaces resistance to mechanical stresses. This study investigates the applicability of a well-known glass hardening process to glazed ceramic tiles following a rational design based on Design of Experiments technique. A Mixture Design has been carried out to formulate new frits compositions to enhance the ion exchange process, starting from a commercial product. Vickers Hardness and SEM-EDS techniques have been employed to evaluate the frits and elaborate the model. Results suggest that frits for ceramic tiles are positively affected by ion exchange process only if an appropriate combination of ions in the starting composition is present, establishing a new category of frit formulations suitable for that purpose. The

results have been confirmed employing the optimized frit for the glazing of porcelain stoneware.

1 Introduction

Ion exchange (IE) is used since about a century to modify the surface properties of glasses. Over the years, IE processes have been developed and industrialized for multiple applications, including the production of glasses with high mechanical strength and electrodes with high resistance to chemical attack [1-4]. Others processes improvements have been developed to work for components with different shapes, such as curved or wavy, and with very small thicknesses, such as Gorilla Glass™ by Corning®, thus avoiding the problems of other technologies, such as optical distortion on the surface or premature failure [5-6]. Chemical tempering is an IE process for strengthening based on the diffusion of larger cations from a molten salt bath to the glass network, exchanging with smaller cations which diffuse in the opposite direction. In the most common configuration, silicate glasses containing alkali ions such as Na^+ or Li^+ ions are immersed in a bath of KNO_3 in the range of 400 °C and 500 °C, for several hours (4-120h) [7-9].

Many studies have been performed to investigate the role of the glass chemical composition on the efficiency of the process. The main result of these studies suggests that the glass alkaline content should be relevant (>10 mol%) to make effective the ion exchange. Moreover, the presence of monovalent cations (K^+) in the starting glass composition promotes the diffusion due to the "Mixed Alkaly Effect" and divalent cations limit the ions movements [10-12]. Furthermore, aluminosilicate glasses are the most promising due to the presence of (Al^{3+}) that in tailored conditions is able to promote the alkaline diffusion [13-15].

Finally, others glass formers such as B_2O_3 and P_2O_5 could promote local environments favoring the ~~cations~~ diffusion of cations [16].

Previous studies have shown that standard ion exchange processes can be employed to increase up to ~74% the flexural strength of unglazed porcelain stoneware avoiding any subcritical growth of cracks during cooling [17]. Related studies also demonstrated that the chemical and mineralogical compositions of the porcelain stoneware are the most ~~significative~~ significant variables, together with the process temperature, and therefore the increase of flexural strength is successfully promoted by a restrained crystalline phases content into the porcelain stoneware [18].

In ceramic tile production glazes have the main role to protect the porcelain stoneware from chemical attacks, covering all the open porosity, but interest is growing about the glaze hardening to overcome the critical issues of such fragile materials. In fact, ceramic glazes are mainly composed by special types of glass, known as ceramic frit, obtained through very fast quenching of glass by immersion in water [19]. Nowadays IE may be considered as possible route to perform hardening of glazed porcelain stoneware, improving the properties and the efficiency of thin products, according ~~with~~ to the environmental requirements for floor and wall coverings needed for green building, as stated in the European Union Decisions 2009/607/CE establishing the ecological criteria for the award of the Community Eco-Label to hard coverings [20]. One of the main drawbacks of this approach is that the chemical formulation of a ceramic glaze is even more complex than the formulation of a glass because typically contains a higher number of oxides, that surely interact among them. Moreover, generally, the employment of Na^+ is reduced to avoid strong decreases of the glass transition temperature, generating defects during the fabrication process [19].

This study is focused on the comparison among different glaze formulations, undergoing to a chemical tempering process, to quantify correlations between glaze composition and hardness

of the glazed porcelain stoneware. To achieve this goal the study has been organized in two main parts: in the first, a commercial glaze has been considered and its behavior to chemical tempering have been tested, also after application on porcelain stoneware, in terms of Vicker hardness (HV), scratch resistance, physical and microstructural properties. The second part concerns new frits formulation by using the Mixture Design approach as a tailored tool of the Design of Experiments method that allows quantifying how each component and its potential interaction with others affect the final performance of the material [21]. The application on porcelain stoneware of the best glaze deriving from the frit optimized by Mixture Design has also been tested. ~~The~~ Process parameters have been maintained constant to focus our attention only on the glaze composition role. The innovative results obtained lead to propose a glaze composition, containing a complex combination of oxides with respect to a typical glass composition, in which IE attitude is emphasized and therefore the surface chemical hardening promoted, leading to glazed porcelain stoneware with improved mechanical performances.

2 Materials and Methods

2.1 Preparation of the samples

2.1.1 Industrial glaze

The industrial glaze was prepared starting from an industrial frit, selected overall the main groups of commercial frits due its high content of Na^+. This glaze is generally employed for low thickness application in the porcelain stoneware production [22]. The measured composition of the industrial frit is $54SiO_2$-$13B_2O_3$-$8Al_2O_3$-$12Na_2O$-$6CaO$-$5MgO$-$2K_2O$ mol%. The frit was ~~grinded~~ ground in an agate mill for 20 min to obtain a fine powder (ca. 32 micron) suitable for the thermal analysis. In order to investigate the bulk materials by SEM-

EDS characterizations, 25g of frit was melted in platinum crucibles at 1550 °C for 30 min. Subsequently, the melt was casted into a cubic graphite mold having an internal volume of 1cm^3. Finally, the sample was annealed at 750 °C and let to cool naturally in the turned-off furnace down to room temperature to remove residual stresses from the forming step. The annealing temperature was selected by studying the DSC curve and performing the heating treatment from 10 °C over the glass transition temperature to room temperature. The ground frit was poured into an industrial mill with 20wt% of white clay (kaolin) and water with alumina balls having different diameters. Milling was performed for 30 min. After milling the slurries were wet sieved and the fraction passing through a 400-mesh sieve was taken in account. The slurry was deposited on a dry green porcelain stoneware tile support by airless method and then the each specimen (10x10cm) was fired in an industrial kiln for 50 minutes (cold to cold) reaching the maximum temperature of 1200 °C.

2.1.2 Design of new frits through a Mixture Design approach

The compositions investigated in the second part of this study were designed by using the Mixture Design approach in which two main constrains were used: the first regarding the relative proportion of the constituents in the mixture, and the second taking in account the additional boundary constrains on the constituent proportion. This statistical based approach overcomes the strong simplifications intrinsic into the so called One- Factor-at-A-Time (OFAT) outlook, reducing the number of experimental tests needed to provide the maximum information content on complex issues, saving both time and resources [21].

Therefore, to manage this specific experimental region the Computer Aided D-optimal Design was used [21,23,24]. Mixture model forms (MMF), most commonly used in fitting data, are the canonical polynomials known as the Scheffé canonical given by [21,25]:

$$MMF = \sum_{i=1}^{q} \beta_i \cdot x_i + \sum_{i<j}^{q} x_i \cdot x_j \cdot \beta_{ij}$$

where β_i and β_{ij} are regression coefficients calculated from the experimental data by multiple regression, and x_i and x_j are the levels of the independent variables [25]. The analysis of variance (ANOVA) was employed to evaluate the model significance and its predictive power to describe the relationships between compositions and properties. In particular a statistical difference among samples can be defined when the variation among all the samples, usually due to process or factor changes, is larger enough than the variation within samples obtained in the same experimental conditions [25]. The residual analysis was used to point out potential deviating experiments, as well as the regression coefficients were analyzed by the p-value approach: p-values higher than 0.05 were not considered as statically significant and therefore neglected for the model formulation [26,27]. The quality of the fit in terms of regression analysis and the prediction power of the models were evaluated by using the R^2 and Pred-R^2. R^2 is the proportion of the variance in the dependent variables that is estimable from the independent variables and Pred-R^2 is similar to R^2 but calculated through the predicted values of the dependent variables [21]. Design Expert (version 8, Stat-Ease) software was used to the data analysis [28]. Table 1 reports the components considered in this work and their specific range.

Eighteen experiments, including one center points replicated 4 times, were planned. Replicate points allowed estimating the model's lack of fit as well as its reliability. The experiments were performed according to the randomized run order to avoid environmental conditioning. The response contour plot was used as functional tools in explaining the role of the main components on the final property considered.

2.1.3 New frits preparation

Technical grade raw materials were employed in order to obtain frits according to the experimental plan (Table 3). In particular, SiO_2, H_3BO_3, Al_2O_3, Na_2CO_3, $CaCO_3$, MgO, K_2CO_3, Li_2CO_3 and P_2O_5 with purity >97% (the purity is the same of industrial materials) were mixed in batch of 50g, melted in platinum crucibles (heating rate of 10 °C/min from 25 to 1550 °C with a final dwell time of 40 min), and then quenched in water. All raw materials were employed as pure oxides or carbonates to enhance the composition careful control. Therefore, the same procedure applied for industrial frit was employed. The optimized frit as resulted from Mixture Design was taken in consideration as base to produce a glaze and therefore applied with the same methodology mentioned in paragraph 2.1.1.

2.2 IE process

The specimens were completely immersed in a bath of melted KNO_3 at a temperature of 450 °C for 4h employing an industrial kiln (LEMA, TC20A). Subsequently, the specimens were cleaned with hot water to remove any salt residue and dried at 120 °C for 24h. This process was chosen from literature as the most commonly employed for float glass [7-9].

2.3 Experimental Characterization

The characterizations were performed using a multiple techniques approach for frits and glazes. The chemical composition of the industrial frit was obtained by X-Ray fluorescence (XRF, Thermo ARL ADVANT' XP+) and inductively coupled plasma (ICP) analysis, with evaluated error ±0.1 wt%. The thermal behavior of each frits was measured using differential scanning calorimetry analysis (DSC, Netzsch 404) performed in air at a heating rate of 10 °C/min using 30mg of powdered samples. The glass transition temperature (Tg) was

calculated as the cross-point between the tangent on the initial straight line before baseline

shifting and the tangent on the slope. Evaluated error on this measurement is associated with

the sensitivity of the instrument (± 10 °C). This evaluation was necessary to ensure the IE

process temperature below Tg, to retain the vitreous structure of the glass.

The cross-sections of frits and glazed porcelain stoneware, polished with diamond papers,

were observed using scanning electron microscopy (ESEM, FEI Quanta 200) equipped with

an energy dispersive X-ray spectroscopy device (EDS, Oxford INCA-350). Considering that

the ion exchange is a near-surface process, the results should display a difference in ions

concentration along the cross-section. Therefore, the semi-quantitative chemical analysis of

the cross-section was conducted through punctual EDS measurement, made every 5 μm from

the border to the core of the ion exchanged surfaces, to identify changes in ion concentration,

avoiding any interference between two near measurements due to the magnification

employed. The voltage of the electron beam was reduced as much as possible, working at 5

kV, to avoid the mobility of light alkali ions under the electron beam. This measurement

procedure was performed on at least five different areas of the same sample for ten times to

evaluate standard deviations. Ion Exchange Depth (IED) parameter was evaluated as the

distance from the surface of exchange to the core, throughout a higher amount of K^+ with

respect to the amount of Na^+ was detected. It is worth noting that this method was already

successfully used in previous studies on ion exchange process in glasses, therefore useful

conclusions can be reasonably drawn also for the frits analyzed in this work [29-31]. HV of

the frits and glazes porcelain stoneware was measured before and after the ion exchange

process using a micro Vickers hardness (Wolpert, Micro Vickers tester 402-MVD) with a

constant load of 0.5 kgf and dwell time of 15 s. This load was selected as a result of several

preliminary tests performed to derive the highest load of penetration possible, avoiding the

crack formation near to the border of the footprint. Twenty indentations were performed on

each specimen and the results were indicated as average ± standard deviation. The indentations were performed on cubic specimens of molded material for frits and on the glazed layer for porcelain stoneware tiles.

Glazed porcelain stoneware was characterized through X-ray diffraction (XRD, PW3710, Philips) with Cu-Ka radiation and conventional $\theta-2\theta$ geometry. Water absorption (AA) was performed following the standard EN ISO 10545, in order to evaluate differences in the microstructure before and after the immersion in the molten salt bath [32].

On these specimens a further mechanical characterizations was were performed through scratch and wear resistance tests. Scratch test (Micro-Combi Tester, Anton Paar TriTec, Peseux, CH) was carried out using a Rockwell C-type conical diamond indenter having a 200 µm-radius spherical tip and operating with linearly increasing load ("progressive-mode scratch test") from 0.01 N to 30 N. Scratch length and speed were 6 mm and 1 mm/min, respectively. Three tracks were performed on each sample. Visual inspection of the track by optical microscopy allowed defining the critical loads for the onset of specific damage mechanisms. In this study the critical load taken in account was due to the flake-off of the glaze (L_{c2}) following ISO 20502 procedure [33]. Wear resistance test was performed on ball-on-disk geometry (High-Temperature Tribometer, Anton Paar TriTec) according to ASTM G99 [34]. Specifically, glazed samples were tested against a 6 mm-diameter alumina ball. Test conditions included a constant normal load of 5 N, a relative sliding speed of 0.20 m/s and a total sliding distance of 500 m. Three repetitions were performed for each specimen and therefore the differences in weight before and after the test were considered to evaluate the wear. All the weights were measured with analytical balance with sensibility of 10^{-5} g. All tests were run in replicate for each coating, at 25 °C with 60% relative humidity.

3 Results and Discussion

3.1 Industrial frit

The aim of the thermal analysis was to investigate the glass transition temperature (Tg) of the industrial frit. The melting temperature of the salt bath employed during the IE process (450 °C) must be below the Tg of the frit, in order to avoid any uncontrolled change in the network structure and the softening of the frit during the IE process. DSC results (Figure 1) clearly show that the industrial frit can be tested for IE process employing a temperature equal to 450 °C because the Tg is equal to 590 °C. Moreover, also the annealing temperature of the bulk specimen selected equal to 750 °C, as previously discussed (2.1.1), is confirmed to stands over the Tg. Finally, no crystalline peak is visible in Figure 1 therefore no crystallization is expected due to thermal treatments, therefore, the frit can be classified as glossy.

The EDS results (Figure 2) highlight that industrial frit can be successfully treated with IE. Considering that this process is a near-surface activity, the occurrence of IE in this sample is highlighted by an inversion of the concentration of the two ions close to the reaction zone. In particular, the K^+ concentration is higher at the surface and lower near the core of the sample, whereas the opposite is observed for Na^+ confirming the IE process. The IED parameter, according to the definition stated in paragraph 2.3, is about 10 μm.

The effective hardening of the industrial frit has been confirmed by hardness measurements as shown in Table 3 where the HV before and after the IE process ~~have~~ has been measured. Considering the calculated error associated to the HV measurements it is possible to conclude that the comparison of the average values is statically reliable and point out a substantial increasing of HV after IE process. SEM measurements reported in Figure 3 show~~s~~ a slight, but significant, decreasing of the measured indentation after IE and this is consistent with the calculated HV which speaks about a hardened glass by IE process. In Figure 3 it can be also observed the absence of cracks or relevant surface defects before IE suggesting a very good

performance of the annealing treatment. According to results from literature about glass, a content of $Na^+ > 10\%$ and the absence of crystalline phases ensure a successful IE treatment for frit, nevertheless a more complex formulation of oxides is treated.

3.2 Industrial glazed porcelain stoneware

As shown in Table 2 the results obtained for the industrial frit can be achieved also for the industrial glazed porcelain stoneware; In fact, a significant increase of hardness, wear and scratch resistance can be obtained. Considering Table 3 the HV parameter increases significantly after the IE treatment, reaching the final value of 0.68 GPa, in strong similarity with the general results from industrial frit characterization. The HV values obtained for glazed porcelain stoneware are significantly lower than the ones obtained for frits due to different chemical compositions, in fact as stated in paragraph 2.1.1 the glaze composition includes frit and clay. Moreover, due to the difference in coefficient of thermal expansion between glaze and porcelain stoneware support (data not reported) the applied glaze is naturally affected by a stress state after cooling, with respect to a bulk material (as in the case of frits), and this is consistent with the lower obtained values. Taking in account the further mechanical characterizations, the scratch resistance has been evaluated as the critical load that is necessary to remove the outer part of the glaze from the support (L_{c2}) and therefore the value obtained after the IE treatment, as reported in Table 3, suggests that this load must be increased. All the traces of the scratch tests reported are characterized by tensile-type Hertzian circular cracks with spallation inside the trace, as shown through optical microscopy observations (Figure 4) where the effects of the test final load (30N) has have been show. This load has been chosen as the highest achieved during the test, consequently, the expected effect on the surfaces and scratch property is reasonable the most critical, due the inverse proportion between load and scratch resistance property. In Figure 4a the glaze surface before

IE is hardly damaged, and a relevant part of the glaze is detached from the porcelain stoneware; on the opposite, in Figure 4b the glazed surface after IE is shown, and a less damage surface is present.

In strong similarity with the other analyzed properties, the wear resistance, indicated in terms of amount (%) of material removed during the ball-on-surface test, strongly decreases after the IE treatment. In fact, a reduction of material loss from 0.09% to 0.05% is registered for the industrial glaze. Nevertheless, a difference of 0.04% could seems insignificant it must be considered that this quantity is estimated taking in account the weight of all the glazed porcelain stoneware specimen, therefore the percentage related to only the glaze weigh is significantly higher.

Finally, about glazed porcelain stoneware, also microstructure and water absorption have been evaluated to ensure any undesired modification of the support due to the treatment in the molten salt bath. For first, the water absorption has been considered and, as shown in Table 3, this parameter does not change significantly, confirming that open porosity of the porcelain stoneware is unvaried. The same result is confirmed by the XRD analysis performed on the porcelain stoneware support where the same crystalline phases have been identified before and after the IE process with very similar intensities of the peaks (Figure 5). It can be concluded that the industrial frit is suitable to answer to the requirements of chemical strengthening by using IE and therefore the Mixture Design can be focused on it, as base to derive a potential new glaze formulation.

3.3 New frits from mixture design analysis

The ranges of compositions selected for the Mixture Design investigation are detailed in Table 1 from which the experimental plan of Table 3 has been derived. On the right of Table 3 are reported the measured parameters (Tg, HV, ΔHV, IED) for each frit obtained. The

estimated error on the glass transition temperature is ±10 °C for each experiment and it results statically reliable. As shown from Table 3 all the glass transition temperatures are included in the range 530-610 °C and both the annealing point of 750 °C and the ion exchange process temperature of 450 °C can be employed for this group of specimens, in strong similarity with industrial frit. HV parameter has been measured after the application of the IE process and also the HV variation (ΔHV) has been taken in account as the difference between final HV and HV before the IE process. HV and ΔHV data have been analyzed by the ANOVA and leads to very similar results, therefore only the data analysis for ΔHV has been reported hereafter. The ΔHV parameter has been considered to overcome the possible uncertain since, even if below Tg, the same IE temperature can produce different effects in different frits, according to the distance from their glass transition temperature. About the calculated average values of IED, HV and ΔHV the estimated errors fall in the range of 5% for each experiment allowing a statically reliable comparison among data.

he ANOVA results in Table 4 shows that the two F tests are satisfied: F-value is higher than one (equal to 191.6) with a p-value < 0.05, and the lack of fit is not significant with a p-value > 0.05, allowing to conclude that the model is significant. Moreover, R^2 and Pred R^2 point out the excellence of the model validity with values very close to 1.00, which explain a reliable correlation between glass composition and ΔHV. The normal distribution of the residuals has been analyzed (data not reported) confirming that the model can be used to explore the region of interest. The resulting model allowed to describe the relationships between compositions and the final measured responses as shown in the calculated regression (eq.2).

$$\Delta HV = -7.16978 * B_2O_3 - 1798.9514 * P_2O_5 - 8.60007 * Na_2O - 172.5346 * Li_2O +$$
$$1813.51071 * B_2O_3 * P_2O_5 + 39.27082 * B_2O_3 * Na_2O + 481.3966 * B_2O_3 * Li_2$$
$$+ 1858.88634 * P_2O_5 * Na_2O + 1081.00785 * P_2O_5 * Li_2O + 419.15942 * Na_2O *$$
$$Li_2O + 289.68752 * B_2O_3 * P_2O_5 * Na_2O + 172.12578 * B_2O_3 * P_2O_5 * Li_2O -$$
$$1144.66549 * B_2O_3 * Na_2O * Li_2O + 2155.14629 * P_2O_5 * Na_2O * Li_2O$$

The analysis of the coefficients of the models suggests that single factors but also their interactions contribute to explain the correlation between composition and ΔHV as shown in Figure 6 (a). In figure 6 (a) and Figure 6 (b) the Li_2O content has been fixed equal to 2 wt% due to the restrained number of components comparable in a surface response graph and considering that the selected amount of Li_2O generates the largest area of the response surface. In fact, a further increasing content of Li_2O over 2 wt% leads to a decreasing of ΔHV (data not reported). Therefore, the following part of the analysis has been focused on the others three more significant factors.

Considering the main singular effects, the most significant one is P_2O_5 in fact an increase of P_2O_5 content from the minimum to the middle value produces an increase of the ΔHV, but a further increase of P_2O_5 content up to 3wt% leads to a restrained decrease of ΔHV. This trend is consistent with the already known role of P_2O_5 as both glass former or modifier, according on type and amount of other oxides in formulation [16]: for the series of frits studied in the present work the increasing of the P_2O_5 acting as modifier promotes the network depolymerization which results in a high tendency of cations to move, favoring the IE; when the P_2O_5 content further increases the network former role start to take place and therefore the high glass interconnectivity starts to reduces the ions mobility and then the IE effectiveness. At the same time, an increase of Na_2O or B_2O_3 content leads to a decrease of ΔHV. Concerning the B_2O_3, its network former role results in a more packed structure at high concentration that limit the IE, in similarity with P_2O_5. Na_2O effect is stronger than the one observed for B_2O_3 and suggest that Na^+ content have not to be increased over the 10wt% in order to retain a high ΔHV. Moving toward higher values in Na^+ concentration results in a

strong interference in the diffusive path of the high percentage of exchanging ions. A similar behavior can be supposed for Li_2O that, in fact, follows the same trend of Na_2O and any increasing over 2wt% should be avoided (data not reported).

Also, the interaction effects have been examined and the main results have been reported in detail in Figure 6 (b). It can be highlighted that an intermediate content of each oxide should be selected in order to enhance ΔHV. From this compositional analysis, it can be stated that enhanced hardening by IE can be reached considering a restrained range of wt% of each component due to the strong interaction among oxides in a complex formulation such as industrial frits. The composition of the optimized frit, considering only the variated factors, results equal to $13.5B_2O_3$-$1P_2O_5$-$10.5 Na_2O$-$2Li_2O$. A rational approach such as Mixture Design allowed to point out how small changes in composition can yield considerable results in practice due to the structural transition, occurring when interaction among a large number of components takes place.

The statistical analysis for IED is not reported since the model is not significant due to high pure error. Taking in consideration the ranges of formulations reported in the Mixture Design is confirmed that the EDS method allows only to derive semi-quantitative information on the ion exchange process applicability or not.

3.4 Optimized frit and glazed porcelain stoneware

Optimized frit ($13.5B_2O_3$-$1P_2O_5$-$10.5 Na_2O$-$2Li_2O$) applied on porcelain stoneware, has been characterized following the same procedure performed for the starting materials (industrial frit and glaze). Therefore, a comparison can be made not only before and after the IE process but also before and after the Mixture Design optimization of the chemical formulation of the frit. Considering the frits characterization, as shown in Table 2, the IED parameter results

unchanged after the mixture design optimization, even if a significant increment of HV average value after the IE process is detected up to +40% employing the optimized frit (6.3 GPa) instead of the industrial one (4.5GPa). Again, the IE process results promoted by the optimized frit considering that the HV difference between the optimized frit before (3.8GPa) and after the IE process (6.3 GPa) is equal to 2.5 GPa and therefore larger than the same difference evaluated for the industrial frit and equal to 1.1GPa (before IE is 3.4 GPa and after IE is 4.5 GPa). This trend is also in agreement with the restrained errors on the measured average values. The mechanical properties of the glazed surface investigated suggest that the results drawn for the frits are confirmed, taking in consideration the scratch and wear resistance tests. The scratch resistance of the optimized glazed surface results improved of about +150% after the IE process: the scratch resistance measured before the IE process is equal to 4.8 N and after the IE process is 12.3 N. This means that to produce the same damage on the surface it is needed +150% of the load, or in other terms the same load produces less damage, as shown in Figure 4: a load of 30N produces a very restrained spallation for the optimized glaze (Figure 4d) with respect to the industrial glaze after the IE (Figure 4b) and to the optimized glaze before IE (Figure 4c). The wear resistances obtained for the optimized glaze shows a difference of 0.04% from before to after the IE process, very close to the one observed for the industrial frit, nevertheless is evident that for the former the ranges are around lower values of material loss. About glazed porcelain stoneware characterization, it must be noted that the IE treatment does not have a negative impact on the microstructure of the porous part of the material, in fact water absorption (AA%) and XRD pattern are in practice the same. This is due to the fact that the porcelain stoneware is, for its nature, a material with a very low amount of open porosity, therefore the possible salt residues are not able to penetrate the microstructure.

4 Conclusions

In this work functional relationship between the composition of frits suitable for porcelain stoneware production and their hardness, obtained through an ion exchange process, has been determined using Mixture Design approach. In the first part of this study a commercial frit for porcelain stoneware has been characterized and treated through a well-known ion exchange process established for chemical hardening of glass. This treatment has positive effect on improving the frit hardness, although frits for porcelain stoneware ~~has~~ have a more complex oxide formulation than a general float glass. As a consequence, this industrial frit resulted the best candidate for the Mixture Design study in order to explore a compositional range suitable to find a tailored frit formulation. In particular the content of B_2O_3, P_2O_5, Na_2O_3 and Li_2O have been varied pointing out that the interactions between oxides concentration play a fundamental role in new frits design for technological applications. In this study compositions in which P_2O_5 is present at most within 1wt%, the Na_2O at most within 10.5wt%, the B_2O_3 at most within 13.5wt% and Li_2O 2wt% promoted frits characterized by higher HV.

This result is confirmed after application of the frits as glaze on porcelain stoneware: for the optimized formulation an increase of the HV (+40%), of the scratch resistance (+150%) and of the wear resistance (+130%) can be highlighted by applying the IE process, allowing to confirm the effective potential application of this chemical strengthening method also for industrial ceramic tiles products.

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Figure 5. Comparison of the XRD pattern before (red) and after (blue) the IE process. Identified crystalline phases: Quartz (Q) ICCD:01-083-0539 (SiO_2); Mullite (M) ICCD: 01-079-1454 (Al_5SiO_9); Albite (A) ICCD: 00-001-0739 ($NaAlSi_3O_8$)

Figure 6. (a)Variation of ΔHV through 3D response surface of the system (A-B-C) B_2O_3-P_2O_5 -Na_2O ($Li_2O=2$ wt%) (b) focus on a 2D slice in correspondence to $\Delta HV=2.4$. All quantities are expressed in wt%

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Table 1

Name	Low level (-1)	High level (+1)
B_2O_3	10	15
P_2O_5	0	3
Na_2O	10	15
Li_2O	1	5

Table 2.

		IED (μm)	HV (GPa)	Scratch resistance (N)	Wear (%)	AA %
FRITS	INDUSTRIAL					
	Before IE	0	3.4±0.3	/	/	/
	After IE	~10	4.5±0.2	/	/	/
	OPTIMIZED					
	Before IE	0	3.8±0.3	/	/	/
	After IE	~10	6.3±0.2	/	/	/
GLAZED PORCELAIN STONEWARE	INDUSTRIAL					
	Before IE	0	0.52±0.01	3.4±0.2	-0.09±0.01	0.37±0.12
	After IE	~10	0.68±0.01	7.9±0.2	-0.05±0.01	0.16±0.04
	OPTIMIZED					
	Before IE	0	0.69±0.01	4.8±0.2	-0.07±0.01	0.40±0.10
	After IE	~10	0.81±0.01	12.3±0.2	-0.03±0.01	0.18±0.05

Table 3.

RUN	B_2O_3 wt(%)	P_2O_5 wt(%)	Na_2O wt(%)	Li_2O wt(%)	Tg (°C)	IED (μm)	HV (GPa)	ΔHV (GPa)
1	11.7	0.0	13.0	2.3	550	2	4.41	+0.84
2	12.3	1.5	10.5	2.7	570	2	6.20	+2.64
3	13.3	0.0	12.7	1.0	530	0	4.92	+1.40
4	15.0	1.0	10.0	1.0	610	20	6.10	+2.55
5	10.0	0.0	15.0	2.0	520	5	4.57	+0.98
6	11.3	1.5	11.5	2.7	575	0	6.25	+2.74
7	11.0	3.0	12.0	1.0	630	0	5.72	+2.11
8	11.0	3.0	10.0	3.0	610	4	5.47	+1.97
9	15.0	0.0	10.0	2.0	600	3	5.52	+1.99
10	10.0	1.0	13.0	3.0	540	7	6.33	+2.76
11	12.3	1.0	11.0	2.7	580	10	6.30	+2.64
12	10.0	1.5	10.5	5.0	560	7	5.20	+1.61
13	13.0	0.0	10.0	4.0	595	0	5.44	+1.91
14	10.0	3.0	13.0	1.0	605	4	5.74	+2.16
15	13.0	3.0	10.0	2.0	600	10	5.49	+1.93
16	10.0	0.0	12.0	5.0	530	0	4.23	+0.67
17	11.0	1.0	10.0	5.0	570	10	6.13	+2.57
18	12.3	1.5	10.5	2.7	575	15	6.26	+2.65

Table 4.

F-test	p-value	Lack of fit test	p-value	R^2	Pred R^2
191.6	<0.0001	3.91	0.15	0.98	0.92

a)

ΔHV

Na₂O

P₂O₅

B₂O₃

b)

B₂O₃ =15
Na₂O=10
P₂O₅ = 0

B₂O₃ =13.5
P₂O₅ = 1.0
Na₂O=10.5

P₂O₅ = 3
Na₂O=10
B₂O₃ =10

Na₂O=15
B₂O₃ =10
P₂O₅ = 0