# QUANTIFICATION OF PHASES IN REFORMULATED COMPOSITIONS OF PORCELAINIZED STONEWARE TILE

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## 1. INTRODUCTION

While natural ceramic raw materials are getting scarce, hence more expensive, the use of alternative raw materials becomes interesting, both technically and economically. However, the use of replacement materials entails a sometimes thorough reformulation of mixture compositions so that the final product keeps its characteristics. Although in normal industrial operating conditions thermodynamic equilibrium is usually not reached, much of that reformulation work can still be guided by a trained use of phase diagrams.

During the reformulation work, the "natural" tendency is to simply replace the content of the original raw material by an equal amount of the alternative material (or of a mixture of the two). By doing so, and because their compositions are often far apart, the final product composition changes (*i.e.* moves in the phase diagram), the content of liquid phase formed during firing changing with it. Such a hasty reformulation might end up leading to a complete failure of the desired product. This work illustrates this procedure through the phase quantification in porcelainized stoneware tile compositions, such as found in the literature and after reformulation. In the latter case, the feldspar, which is the major raw material used to fabricate this type of product, was replaced by a synthetic glassy phase former.

## 2. EXPERIMENTAL PROCEDURE

The selected composition was that of a typical industrial product, formulated using conventional raw materials of known chemical composition. That theoretical composition was then modified, the 45% feldspar content being partial or totally replaced by a synthetic glassy phase former (flux). After firing, the compositions were characterized by X-ray diffraction (XRD) to identify the phases present. The amounts of the phases present in the fired compositions were calculated using the chemical composition data, the lever rule and the relevant phase equilibrium diagram, on the one hand, and the XRD data and the Rietveld method (*software* Fullprof 2000), on the other hand. The results obtained by the two methods were then compared and a new formulation (NF) was prepared, without feldspar but having a phase distribution similar to that of the industrial product.

## 3. RESULTS AND DISCUSSION

The chemical analysis results showed that the natural raw materials and the synthetic flux, as well as their mixtures and the industrial product, all contain alumina ($Al_2O_3$) and silica ($SiO_2$) as major components. Other oxides are also present, such as CaO, MgO, $K_2O$ and $Na_2O$, which act as fluxing agents: when added to the $Al_2O_3$–$SiO_2$ system, these oxides lower the initial melting temperature and promote the development of the liquid phase. The fluxing effects of $K_2O$ and $Na_2O$ are very similar (very similar phase diagrams with $Al_2O_3$ and $SiO_2$). The effect of the alkaline-earth oxides, even if present at low levels, should be added to that of the alkali oxides. Given that $K_2O$ leads to liquid phase formation at lower temperatures and with lower viscosities, the fluxing oxides effect on the $Al_2O_3$–$SiO_2$ system can be best discussed in terms of the phase diagram of the $Al_2O_3$–$SiO_2$–$K_2O$ system, using the joint ($K_2O$+$Na_2O$+CaO+MgO) content as "equivalent $K_2O$" content.

Figure 1 (A) shows the wide difference in the compositions of the feldspar and the flux, as well as the changes in the mixture composition as the flux gradually replaces the feldspar. All mixtures lie in the $3Al_2O_3.2SiO_2$–$SiO_2$–$K_2O.Al_2O_3.6SiO_2$ compatibility triangle (Figure 1 (B)), in which melting starts at 985 °C, and in all of them mullite and feldspar are in equilibrium with the first liquid. However, the amount of liquid formed at that temperature changes from ~61% without flux, to ~39% without feldspar (liquid phase tie-lines are shown in Figure 1 (B) and the calculated amounts are in Table 1). But more important is the striking difference in complete melting temperatures (hence, the melting range), which decreases sharply as the feldspar is replaced by the flux (from ~1700 to ~1200°C, respectively). This has obvious implications during firing (*e.g.* pyroplastic deformation and sagging of the ware).

*Figure 1. (A) Location of feldspar and the flux in the $Al_2O_3$–$SiO_2$–$K_2O$ phase diagram, as well as the mixtures in which the flux gradually replaces the feldspar; (B) first melting tie-triangle (shaded area) and liquid tie-lines.*

| Composition | 100% feldspar | 50% flux+50% feldspar | 100% flux | New formulation (NF) |
|---|---|---|---|---|
| Amount of liquid (wt. %) | 61 | 45 | 39 | 60 |

*Table 1. Estimates of the amounts of liquid phase at first melting, calculated using the lever rule.*

At the actual firing temperature the liquid phase content will be comparatively higher in all the mixtures (*i.e.* the same reasoning applies). During furnace cooling, the third solid (*i.e.* silica) will tend to crystallize out of the liquid phase but some of the latter will remain as a glassy phase.

Based on the above, a new formulation (NF) was prepared with 30% flux (no feldspar), having a phase distribution similar to that of the industrial product (Table I). The characterization results shown in Table II reflect the multicomponent composition (anorthite is present instead of potash feldspar) and the departure from equilibrium cooling (four phases present). A rather good agreement can be seen between the calculated amount of liquid phase (~60%) and the joint amount of quartz + glassy phase (23.9% + 40.2%, respectively).

| Phase | Mullite | Anorthite | Quartz | Glassy phase |
|---|---|---|---|---|
| Amount of phase (wt.%) | 16.2 | 19.7 | 23.9 | 40.2 |

*Table 2. Amounts of phases present in fired NF composition (XRD and Rietveld method).*

Despite the short firing cycle, expected to be not long enough to ensure the full establishment of phase equilibrium, the theoretical study using of the phase diagram was found to be very effective in producing good estimates of phase quantities, later confirmed by the experimental results obtained by the Rietveld method. As added advantage of the use of the alternative fluxing agent, further characterization results of composition NF showed that firing can be carried out at a temperature some 50°C lower, and still reach the required low water absorption, with decreased firing shrinkage and good flexural strength.

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