Control of the amorphous content in traditional ceramics by means of alternative fluxing agents

Monica Dapiaggi [a,*], Alessandro Pavese [a], Alberto Maffioli [a], Valeria Diella [b],
Fernando Francescon [c]

[a] *Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Botticelli 23, 20133 Milano Italy*
[b] *IDPA-CNR National Research Council, via Botticelli 23, 20133 Milano Italy*
[c] *Ideal Standard International – C.O.E. – Ceramic Process Technology, Via Cavassico Inferiore 160, I-32026 Trichiana, Belluno, Italy*

ARTICLE INFO

ABSTRACT

The role of KOH and NaOH as mineralisers in kaolinite-quartz (KQ) and kaolinite-quartz-feldspar (KQF) systems has been investigated, in order to determine how they affect the phase composition of ceramic bodies, and if they can replace traditional flux to boost formation of amorphous phases. Attention was paid to the effects induced by mineralisers on (i) the fundamental ceramic equilibrium reaction between crystal phases and amorphous phase, and (ii) on the morphology of the final ceramic product in terms of secondary mullite habit. NaOH and KOH turn out to be amorphous content boosters, but their efficiency to promote amorphous phases is related to quartz particle size, too. The amorphous component appears at the expenses of mullite and quartz, and an analysis of the formation Gibbs energy demonstrates that an increase in mineraliser content shifts the fundamental ceramic equilibrium reaction towards amorphous formation, though Na differs from K in affecting such transformation.

1. Introduction

In sanitary-ware production, like in other traditional ceramics, the starting mixture (slip) is made of (i) a "plastic" component, (*i.e.* sheet-minerals such as kaolinite and clay), (ii) a "hard" component (usually quartz) and (iii) a flux (often feldspar), this latter promoting the melting at high temperature, so as to produce a ceramic material with a low porosity and a large amorphous content [1]. The used proportions of the various components, which may vary as a function of the technologic properties needed for the final ceramic material, require the firing cycle to be adapted [2] accordingly. Flux has a relevant role in the fundamental reactions of traditional ceramics, influencing the equilibrium between the crystalline (particularly mullite) and amorphous phases [3,4]. The use of alternative fluxes is largely diffused, and encompasses a relevant variety of solutions: from soda-lime glass cullet to lithium-bearing rocks, and eventually to a plethora of recycled materials of various origin [5–8]. The common feature of these materials is the presence of alkali-metal ions, such as Na, K or Li [9]. A daunting challenge for sanitary-ware technology consists nowadays in removing (totally or partially) the flux from the slip formulation, introducing

particular substances that allow one to control the development of an amorphous phase upon firing [10,11]. The use of mineralisers (such as NaOH and KOH) has proven very useful not only in driving the formation of high-temperature silica polymorphs, such as cristobalite and tridymite [12,13], but also in changing the amount of amorphous phase at the end of the heating cycle. Tailoring the final amorphous content is of interest for sanitary-ware technology to achieve a full control of porosity [14], which deeply affects mechanical and thermal properties of a ceramic body [15], and to obtain smooth porcellain-like surfaces [16]. The present paper aims at studying the introduction of KOH and NaOH mineralisers as a function of quartz particle size, in free- and bearing-feldspar systems, and its consequences on the formation of the traditional ceramic phases. In particular, attention is focused on how far KOH and NaOH affect (i) the capacity to tune the amorphous content in the final ceramic body, preserving a traditional firing cycle; (ii) the equilibrium reaction between mullite, quartz and amorphous phase. Such transformation is formally treated by its formation Gibbs energy. The goal of the present paper is four-fold: (i) showing that Na$^+$ and K$^+$ can effectively act as flux agents and replace (even totally) feldspar; (ii) setting the basis to develop alternative and more flexible slip compositions, with respect to the traditional ones, by the introduction of mineralisers; (iii) determining the formation energy in the equilibrium reaction between mullite, quartz and amorphous contents, as a function of the mineraliser

Table 1
Summary of the starting mixtures: Q stands for quartz (followed by a number that represents its d_{50} in µm), K for kaolinite and F for Na-feldspar. Mineraliser/water additions are referred to 2.5 g of starting mixture.

Starting mixture	Mineraliser	Mineraliser (mol)
Q28/Q10/Q4 + K	KOH	0.00758 (or 0.00379 or 0.00189)
Q28/Q10/Q4 + K	NaOH	0.00758 (or 0.00379 or 0.00189)
Q28/Q10/Q4 + K	H_2O	0
Q28/Q10/Q4 + K + F	NaOH	0.00379
Q28/Q10/Q4 + K + F	KOH	0.00379
Q28/Q10/Q4 + K + F	H_2O	0
Q28/Q10/Q4 + K + F	KOH + NaOH	0.00189 + 0.00189

content and of quartz particle size; (iv) characterising the microstructural features of the obtained materials, in terms of primary and secondary mullite [2,17,18]. The introduction of KOH and NaOH requires an appropriate adjustment of the deflocculating agents, given that a change of pH, affecting rheology, takes place in the water suspension that is used to cast slip into molds.

2. Experimental

Two sets of samples were prepared: a simplified ceramic mixture containing kaolinite, Na-feldspar, and quartz (hereafter KQF; with three quartz particle size distributions, *i.e.* PSD), and one containing only kaolinite and quartz (hereafter KQ; with the same PSDs). We used quartz powder samples with PSDs having d_{50} of 4, 10, and 28 µm (see [12,13] for previous use of the same materials). Na-feldspar and kaolinte used here are described by Marinoni et al. [19]. KQ-samples (*i.e.* 50 wt% kaolinite and 50 wt% quartz) were treated with different amounts of mineraliser (0.00758, 0.00379, and 0.00189 mol) using solutions of NaOH and KOH, and with 1.5 ml of water (as a reference). KQF-samples (*i.e.* 50 wt% kaolinite, 25 wt% Na-feldspar and 25 wt% quartz) were treated with (i) 0.00379 mol mineraliser, from the same solutions of NaOH and KOH used for KQ; (ii) a combination of equal amounts (0.00189 + 0.00189 mol) of NaOH and KOH; (iii) 1.5 ml of water (as a reference). All mineraliser/water additions are referred to 2.5 g of starting mixture. A summary of the starting mixtures is shown in Table 1. The total number of investigated blends is 33.

The samples were mixed with the mineraliser solutions to a slip, heated up to a maximum temperature of 1250 °C, in a muffle (heating ramp: 10 °C/min), held for 6 h to achieve equilibrium, and then slowly cooled down to room temperature. The samples were then ground in an automatic zirconia mortar to a particle size smaller than 10 µm.
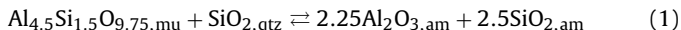
2.1. X-ray powder diffraction

X-ray powder diffraction patterns for qualitative and quantitative phase analyses were collected by a PANalytical X'Pert Pro MPD diffractometer equipped with an X'Celerator detector. Scans for qualitative phase analyses were performed with Cu-Kα radiation at 40 kV and 40 mA, from 5 to 70° 2θ and a counting time of 10 s per step. For quantitative phase analyses, the samples were mixed with a 10 wt% of standard corundum owing to the presence of an amorphous phase, and the diffraction patterns were collected from 5 to 100° 2θ, with a counting time of 50 s per step, using the same settings for the X-ray tube as above. The quantitative phase analyses were then performed by means of the Rietveld + RIR method, as described by Bernasconi et al. [20], for mixtures with large amorphous content, using the software GSASII [21].

2.2. SEM measurements

The micro-structural features of fifteen fired bodies were investigated using a Cambridge STEREOSCAN 360 scanning electron microscope (SEM), with an acceleration current of 15 kV. The samples were previously etched by a solution of 8M fluoro-boric acid for 1 h to remove the amorphous phase and the surfaces were first gold-coated but not polished. The collected images were processed by Image-Pro Plus 4.5 Software, Media Cybernetics Inc., 2001.

3. Formation energy modelling

The equilibrium reaction between amorphous and crystal components at the end of a heating cycle is modelled by

$$Al_{4.5}Si_{1.5}O_{9.75,mu} + SiO_{2,qtz} \rightleftarrows 2.25Al_2O_{3,am} + 2.5SiO_{2,am} \quad (1)$$

in which mullite (mu) and quartz (qtz) provide the crystalline contributions (left-hand side of the equation above), while Al_2O_3 and SiO_2 are supposed to be totally converted into amorphous (am) constituents (right-hand side). We restrict our model to the case of 3:2 mullite, the one occurring prevalently, on the basis of the observed crystal lattice parameters [22] and EDS-chemical analyses [23]. Please note that the output of the firing cycle is here treated as a product at thermodynamic equilibrium, even though the presence of an amorphous phase makes this an approximation. However, this is a reasonable approach, if one considers the time scale, the temperature range, and the reaction kinetics (particularly regarding crystallisation from amorphous) of the processes involved.

Following Adamo et al. [3] and Diella et al. [4], one can write the equilibrium equation below

$$\exp(-\Delta G_{eff}/RT) = \frac{(X_{Al_2O_3,am})^{2.25}(X_{SiO_2,am})^{2.5}}{X_{mu}X_{qtz}} \quad (2)$$

where ΔG_{eff} is the *effective* formation Gibbs energy, which incorporates the temperature dependent contribution and the activity coefficient of the chemical potentials, whereas X_j is the molar fraction of the jth-phase. Each X_j is measured on *ex-situ* samples by powder diffraction. ΔG_{eff}, in turn, can be parameterised as a function of any variable that contributes to fully characterise the system, as shown by the authors mentioned above. Note that here ΔG_{eff} refers to the formation Gibbs energy of an amorphous phase with respect to crystalline phases. In such a light, $\Delta G_{eff} < 0$ means the equilibrium of equation (1) to be shifted towards the right-hand side member, *i.e.* in favour of the amorphous phase. In the present case, we preliminarily explored a thermal interval ranging from 1420 to 1600 K to encompass the T-region of impact upon most traditional ceramics. Then, we chose to focus on T = 1520 K, *i.e.* a reference value for many traditional ceramic firing processes, as the formation Gibbs energy turned out to be weakly sensitive to temperature over the range mentioned above (see also Diella et al. [4], about the role of temperature in such a kind of investigations). In this view, we assumed ΔG_{eff} to be a function of the quartz average particle-size s (see for instance Pagliari et al. [12], about how the quartz size affects the reaction kinetics of cristobalite formation), and of the amount of mineraliser, *i.e.* ξ_{NaOH} and ξ_{KOH} (mol g^{-1}). We therefore parameterised ΔG_{eff} by a straightforward polynomial expansion in s and ξ, as shown below

$$\Delta G_{eff}(\xi_{KOH}, \xi_{NaOH}, s) = \sum_{j=1}^{N} C_j \times \xi_{KOH}^{e1(j)} \times \xi_{NaOH}^{e2(j)} \times s^{e1(j)} \quad (3)$$

where $e1(j)$, $e2(j)$ and $e3(j)$ are exponents related to the jth-term and have to be chosen by a trial-and-error method, in order to provide as best a fitting of equation (2) as possible. Truncation of equation
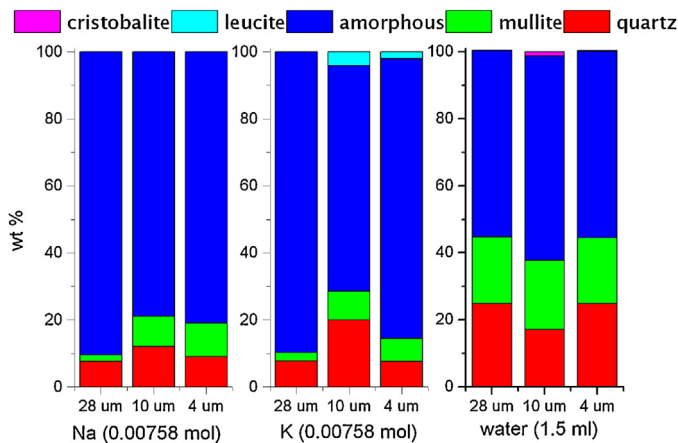
Fig. 1. Influence of the quartz particle size on the samples with a total addition of 0.00758 mol mineraliser (NaOH, KOH), or 1.5 ml water.

(3) was chosen in order to retain only terms whose e.s.d/value ratio is larger than 3.

4. Results and discussion

4.1. KQ-system: samples with no feldspar

KQ-samples were designed with the aim of investigating if and how far the mineralisers can totally substitute feldspar as amorphous content boosters. The samples with added water are then a reference, to which we compare the performances of the mixture with mineraliser.

Fig. 1 shows the results for a given total quantity of mineraliser that corresponds to 0.00758 mol of NaOH, or KOH, and for 1.5 ml of water. The results indicate that the amorphous content increases passing from water to KOH and NaOH (from right to left in Fig. 1), with some samples exhibiting approximately the same amount of amorphous material in the case of both mineralisers. Some samples have over 85 wt% of amorphous phase. Small amounts of leucite (when the mineraliser is KOH) occur; cristobalite forms (in very small amounts) in absence of mineraliser. Quartz is still present, though in varying proportions, in all samples, with the highest residual when the slip contains only water, and the lowest one in the case of NaOH. The highest content of mullite occurs when only water is used. The amorphous phase, when the mineraliser is added, develops at the expenses of mullite and quartz. It is worth noting that the introduction of Na and K ions does not seem to promote the formation of high temperature silica polymorphs, as observed for pure quartz in a previous study [13]. Conversely, the present results are in keeping with the quoted paper in regard to the tendency of forming relevant amounts of amorphous material when mineralisers are used. The influence of quartz particle size on the reactivity of the slip is somehow unusual in the case of Q10, *i.e.* medium d_{50}-value. In fact, Q10 turns out to be the most reactive of Q4-10-28 with water, and the least reactive one with KOH. Q4 and Q28 (d_{50} of 4 and of 28 μm, respectively) share similar behaviours in the case of NaOH and KOH.

A change of the mineraliser total added amount reflects on the phase composition of the samples after firing, as shown by Fig. 2, that displays the results of introducing 0.00379 (Fig. 2a) and 0.00189 mol (Fig. 2b) of NaOH, or KOH. The content of amorphous phase decreases, while the one of mullite increases by decreasing the amount of mineraliser. In particular, the addition of KOH produces the formation of minor quantities of alien phases, such as kalsilite and leucite. A comparison between NaOH and KOH about the phases formation shows that NaOH leads to a larger amount of amorphous phase than KOH does. In general, one observes that the larger the amount of mineraliser, the larger the difference in terms of formed amorphous phase between KOH and NaOH. The difference between mineralisers in affecting the final amorphous content seems to be related to a different proportion of mullite and residual quartz, in the case of 0.00189 mol mineraliser (Fig. 2b), whereas, in the case of 0.00379 mol mineraliser (Fig. 2a), it is mainly ascribable to variations of the residual quartz.

Summarising the effects of changing the amount of mineraliser (Fig. 2), one gathers:

- a reduction in NaOH content decreases the amount of amorphous phase, in favour of quartz and mullite;
- a reduction in KOH content does not change much the relative proportions of the phases. There are small differences in the amounts of mullite and amorphous phase, and residual quartz remains approximately constant;
- a reduction in KOH content totally eliminates the alien phases (leucite and kalsilite).

Fig. 3 shows the variation of residual quartz, while Fig. 4 shows the variation of newly formed mullite, as a function of the total amount of mineraliser added. In both the figures, the size of the symbols is proportional to the d_{50}-values of the starting quartz, with black squares representing NaOH and white rounds standing for KOH.

We can observe the following:

- NaOH. Residual quartz and mullite tend to decrease with the increase of the mineraliser. In the case of residual quartz, Q4 and Q10 show a sort of "saturation" in the range 0.002–0.004 mol of

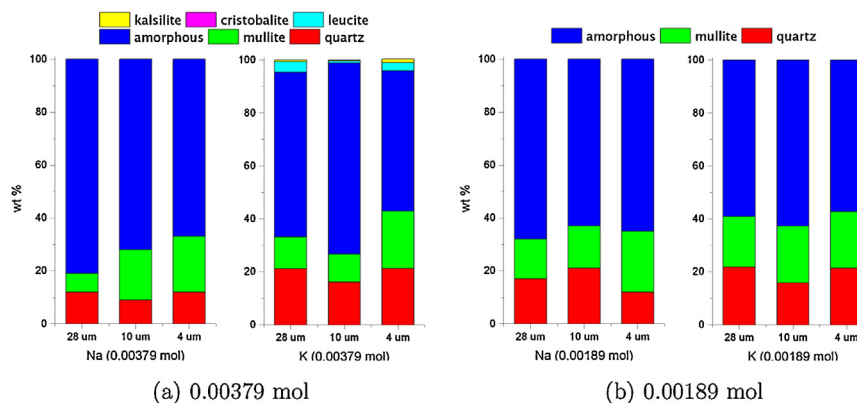(a) 0.00379 mol   (b) 0.00189 mol

Fig. 2. Influence of the quartz particle size on the samples with total additions of 0.00379 mol (a) and of 0.00189 mol (b) mineraliser (NaOH, KOH).
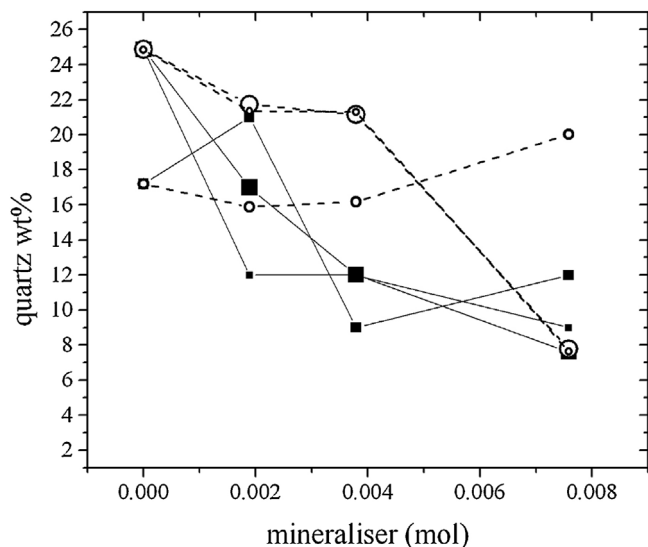
Fig. 3. Influence of the total amount of mineraliser (mol of NaOH or KOH) on quartz formation. The black squares refer to NaOH and the white rounds to KOH; for both mineralisers, the dimensions of the symbols are proportional to the particle size of the starting quartz.

Fig. 5. Influence of the total amount of mineraliser (NaOH or KOH) on the amorphous phase formation. The black squares refer to NaOH and the white rounds to KOH; for both mineralisers, the dimensions of the symbols are proportional to the particle size of the starting quartz.)
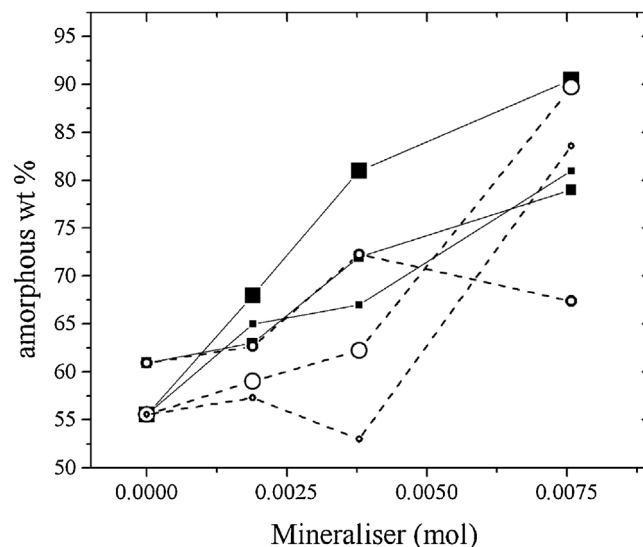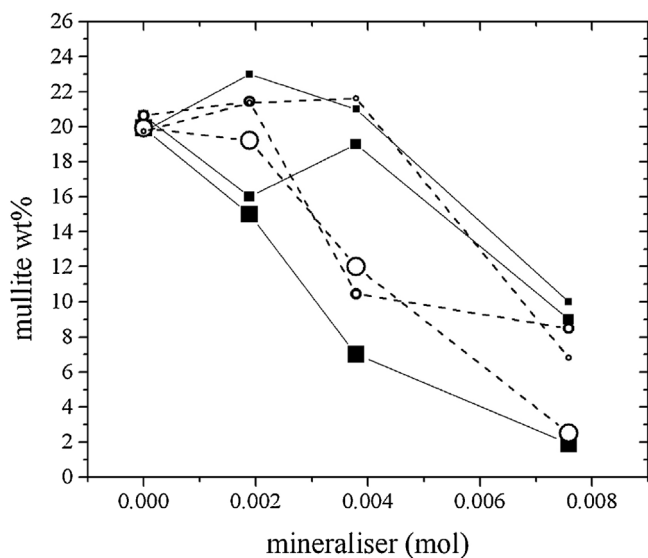
The variations of residual quartz and mullite correlate with the occurrence of the amorphous phase amount, as shown by Fig. 5, where the same symbol key like in Figs. 3 and 4 is used.

The following observations can be made:

- NaOH. The amount of amorphous phase increases from 55 (with pure water) to about 90% wt (with the maximum content of mineraliser). The largest amorphous content is given by the largest particle size quartz, Q28, and all the three quartz samples yield almost monotonical increases of the amount of amorphous phase produced.
- KOH. The maximum amount of amorphous phase is shown by Q28, in presence of the largest mineraliser addition, reaching a value similar to that obtained by NaOH and using the same quartz sample. Q4 leads to a 5–6% wt smaller content of amorphous phase than Q28, with the same total amount of mineraliser. Q10 yields a final amorphous concentration of no more than 67 wt%. The smallest particle size quartz seems to be related to a sort of activation, with no increase of amorphous phase (or with a few wt% decrease) up to 0.005 mol KOH.

4.2. KQF-samples, with Na-feldspar

The set of samples with Na-feldspar, closer to a traditional ceramic slip of vitreous technology, was treated with 0.00379 mol of either mineraliser, 0.00379 mol of a combination of NaOH and KOH in equal molar proportions and 1.5 ml water, as a reference. We chose such mineraliser quantity to achieve an amorphous phase amount typical of a sanitary-ware ceramic body and to investigate how the presence of a traditional flux interferes with the action of a mineraliser. Phase compositions of ceramic products in KQF are shown by Fig. 6.

The behaviour of the sample with KOH does not show a relevant difference with respect to the one with pure water (20–40 wt% of residual quartz and about 45–60 wt% of amorphous phase). The medium particle size quartz, Q10, is the least reactive of the three.

NaOH is more effective in promoting amorphous phase than KOH, and Q4-10-28 exhibit a reactivity that is inversely proportional to their quartz-d_{50}, as one expects.

Fig. 4. Influence of the total amount of mineraliser (mol of NaOH or KOH) on mullite formation. The black squares refer to NaOH and the white rounds to KOH; for both mineralisers, the dimensions of the symbols are proportional to the particle size of the starting quartz.

mineraliser, while Q28 decreases almost monotonically. As for mullite, Q4-10-28 behave differently one from the other in the case of low additions of mineraliser, whereas, for larger amounts, they yield a decrease of mullite, though with different slopes. For both quartz and mullite, the changes are generally not monotonic, *i.e.* there are increases followed by decreases and *viceversa*.

- KOH. Q28 and Q4 give residual quartz amounts whose values almost overlap each other. Q10 provides small changes in residual quartz with increasing mineraliser content, but an increase occurs for the maximum amount of mineraliser used. KOH leads to a larger mullite amount than NaOH, for small additions of mineraliser. Both mineralisers tend to produce comparable mullite amounts, assuming the same d_{50}, upon increasing NaOH/KOH contents.
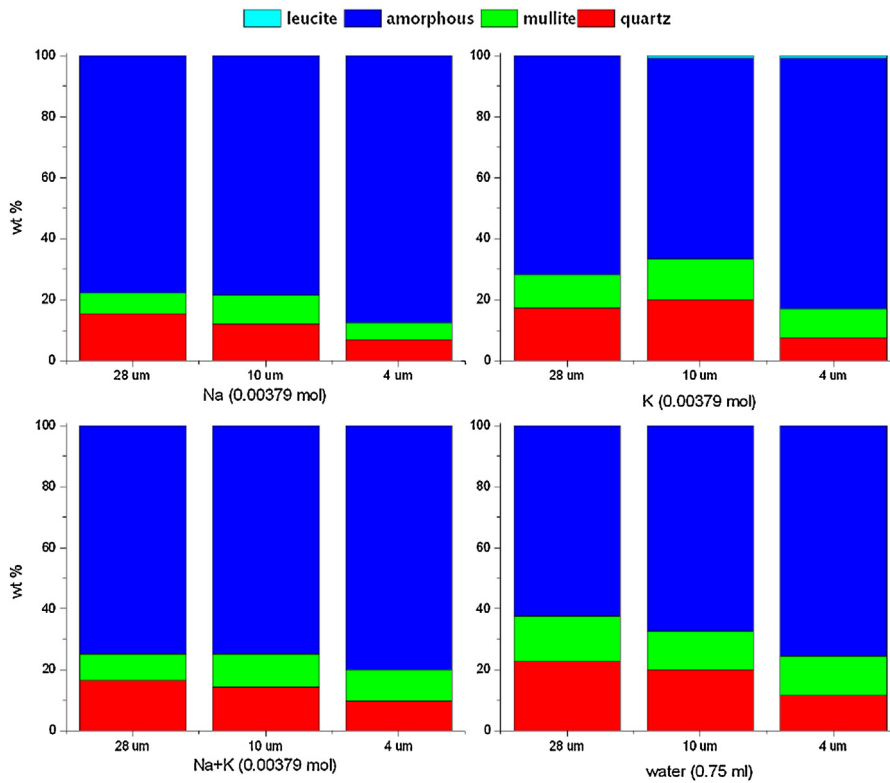
Fig. 6. Influence of the quartz particle size on the KQF-system, *i.e.* samples containing feldspar, with a total addition of 0.00379 mol of mineraliser (NaOH, KOH, NaOH + KOH), or with 1.5 ml of water.

Table 2
C-coefficients of the expansion in equation (3), for the kaolinite + quartz system. C/σ is the coefficient value to its uncertainty ratio. C_0 (kJ mol^{-1}), $C_{1,2}$ (kJ g mol^{-2}), C_3 (kJ mol^{-1} μm^{-1}). s in μm; ξ in mol g^{-1}.

	Parameter value	C_j/σ
C_0	−3.97E+00	7
C_1 (ξ_{KOH})	−4.15E+03	16
C_2 (ξ_{NaOH})	−5.11E+03	24
C_3 (s)	−2.758E−01	3

Table 3
C-coefficients of the expansion in equation (3), for the kaolinite + quartz + feldspar system. C/σ is the coefficient value to its uncertainty ratio. C_0 (kJ mol^{-1}), $C_{1,2}$ (kJ g mol^{-2}), C_3 (kJ mol^{-1} μm^{-1}), C_4 (kJ g^2 mol^{-3}), s in μm; ξ in mol g^{-1}.

	Parameter value	C_j/σ
C_0	−2.32E+01	26
C_1 (ξ_{KOH})	−1.93E+03	9
C_2 (ξ_{NaOH})	−1.73E+04	14
C_3 (s)	4.45E−01	13
C_4 (ξ_{NaOH}^2)	1.97E+06	5

The amount of mullite formed with NaOH is less than half the one obtained with the addition of KOH and water. Leucite is always present, when the mineraliser is KOH, in modest amount.

The combination in equal molar parts of NaOH and KOH yields a final phase composition that suggests a negligible correlation between mineralisers.

4.3. Amorphous-mullite equilibrium

In Tables 2 and 3, the values of the C-coefficients of expansion (3) are set out to model ΔG_{eff} as a function of particle size and mineraliser content (moles per g slip). The uncertainties on the coefficients were estimated taking the smallest ones

obtainable by changing the amorphous content within ±5 wt%, which is assumed to be a reasonable maximum error on the amorphous content determination [20], even with large amorphous amounts.

One observes that:

- the relationships between formation Gibbs energy, mineraliser contents and quartz particle size are linear, with a second order dependence on ξ_{NaOH}, appearing in KQF only;
- the C(ξ_{KOH})-coefficients have the same sign, for KQ and KQF. This holds also for C(ξ_{NaOH}). Therefore both NaOH- and KOH-mineraliser produce qualitatively the same effects on the reaction (1), in either system;
- C(ξ_{KOH}) and C(ξ_{NaOH}) < 0, for KQ and KQF, thus showing the mineralisers promote a shift of the equilibrium reaction towards the amorphous component;
- C(s)/σ is small for KQ and KQF, proving that KQ and KQF are weakly sensitive to s, and any inference relying upon such parameter bears a barely qualitative relevance in the present investigation;
- C(s) > 0 in KQF, and C(s) < 0 in KQ. This hints that the larger s the more the crystal phases are favoured, in KQF; the reverse takes place in KQ. Although such an effect is very modest, it might be related to a tendency of feldspar-flux to exploit the surface of large quartz grains as an anchorage from which to originate secondary mullite;
- although the KQFs C-coefficients agree with KQs in terms of sign, with the exception of s, the absolute C-values show significant differences, implying that the presence of feldspar relevantly affects the equilibrium reaction between amorphous and crystalline phases.

Fig. 7a and b shows the $\Delta G_{eff}(s,\xi)$-surfaces for KQ and KQF, using NaOH and KOH. In the case of KOH, KQ-$\Delta G_{eff}(s,\xi_{KOH})$ and
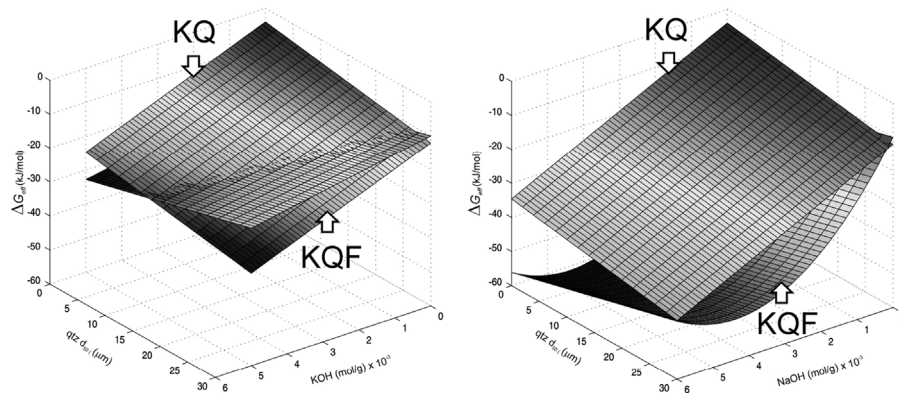
Fig. 7. ΔG_{eff} (s,ξ)-surfaces, for KQ and KQF, using the parameters in Table 2 and 3, as a function of s and ξ. For the sake of calculation, ξ is in mol g^{-1}. The formation Gibbs energy surfaces for KOH (a) and NaOH (b) are displayed.

KQF-ΔG_{eff} (s,ξ$_{KOH}$) surfaces meet one another along an iso-energy line that fixes up the locus of the s-ξ points that affect reaction (1) in such a way that its energetics is independent of the presence of feldspar. Conversely, such surfaces do not intersect each other with NaOH as a mineraliser, which leads to having KQ-$\Delta G_{eff}(s,\xi_{NaOH})$ < KQF-$\Delta G_{eff}(s,\xi_{NaOH})$, thus indicating that feldspar shifts reaction (1) definitely towards amorphous content. In general, $\Delta G_{eff}(s,\xi)$ is more sensitive to ξ than s, as it is inferred from Fig. 7a and b and by inspecting Table 2 and Table 3.

4.4. Morphology of the products

Fifteen samples were investigated by Scanning Electron Microscopy, to determine the morphology of the crystalline products: the reference ones with H_2O for KQ (Q4-10-28) and KQF (Q4-28); those treated with 0.00379 mol mineraliser (NaOH and KOH), for KQ (Q4-10-28 for KQ) and KQF (Q4-28). Mullite is classified as a function of its aspect ratio, *i.e.* length/width: primary mullite, derived from the decomposition of kaolinite/clay, with aspect ratio (1-3:1); secondary mullite, from the reaction among feldspar and kaolinite/clay, with aspect ratio (3-10:1); tertiary mullite, from alumina-rich liquid obtained by dissolution of alumina filler, with very large aspect ratio (30-40:1). It must be taken into account, however, that the size, shape and composition of the mullite crystals are controlled by a variety of factors: (i) firing temperature and time (even primary mullite becomes acicular after prolonged firing times), (ii) fluidity of the local liquid matrix from which they precipitate and grow, (iii) packing degree of the slip and (iv) impurities included in the kaolinite. In this view, the distinction between clay-derived and alkali-fluxed mullites is partially meaningless [2], if complex reactions in multi-phase systems are involved [24].

In Figs. 8 and 9 secondary electron images show the morphology of KQ- and KQF-samples, respectively, using Q4 by way of example.

In the KQ-system, water and KOH give secondary mullite exhibiting average length of 2–3 μm and thickness of about 0.2 μm. In presence of NaOH, mullite reaches a length even up to 10 μm and thickness of 0.3 μm. In full, the observed average aspect ratios are: 10:1, 9-10:1 and 20:1, in samples containing (a) H_2O, (b) 0.00379 mol of KOH, and (c) 0.00379 mol of NaOH, respectively. Crystals of primary mullite exhibit a stocky cuboidal aspect (aspect ratio of 1:1), with length and thickness of 0.1–0.2 μm increasing up to 2 μm in presence of NaOH mineraliser.

The presence of feldspar, *i.e.* KQF-system, reduces the viscosity of the kaolinite-feldspar matrix and favours the growth of mullite needles that are more abundant than in KQ. In KQF-samples, the length of secondary mullite needles ranges from 2–3 to 10 μm, the thickness from 0.2 to 0.6 μm, and the aspect ratio from 10:1 to 20:1.

Table 4
Ω-efficiency values (see text for their definitions) in wt% mol^{-1} g for NaOH and KOH.

System	Mineraliser	Quartz	Mullite	Amorphous phase
QK	NaOH	−4076	−2598	6674
	KOH	−2267	−1943	4210
QKF	NaOH	−3188	−3559	6747
	KOH	−1671	−1122	2793

The largest aspect ratio values generally occur in presence of KOH mineraliser, in contrast with KQ where NaOH is the main booster of aspect ratio. The size of cuboidal primary mullite changes from 0.5, without mineraliser, to 2 μm in presence of KOH.

Comparing the mullite crystals in samples with different quartz particle size and same mineraliser, the average aspect ratios of mullite do not exhibit significant variations.

4.5. Comparison between mineralisers

We introduce the notion of mineraliser's *efficiency* on the *j*th-phase, $\Omega_{miner,j}$, given by

$$\Omega_{miner,j} = \frac{1}{MC} \times \sum_{k=1}^{MC} \frac{(<W_j>_{s,k} - <W_j^0>_s)}{\xi_{miner,k}} \quad (4)$$

where MC = number of mineraliser additions that are taken into account, $<W_j>_{s,k}$ =average over quartz particle size (s) of the content by weight of the *j*th-phase, W_j, in presence of a given mineraliser, whose amount is provided by $\xi_{miner,k}$, *i.e.* mol of mineraliser per g of slip as in equation (3), with the *k*-subscript referring to the *k*th-addition of mineraliser; $<W_j^0>_s$ = average over quartz particle size of the content by weight of the *j*th-phase, without mineraliser. Note that $\Omega_{NaOH/KOH,j} > 0$ means that an addition of NaOH/KOH promotes formation of the *j*th-phase; the reverse in case of $\Omega_{miner,j} < 0$.

In so doing, we obtain the efficiencies that are set out in Table 4. One can observe that:

- efficiency as amorphous phase boosters: the absolute $\Omega_{KOH,amorph}$-values and $\Omega_{NaOH,amorph}$-values behave differently with respect to the presence of feldspar in the reaction; in the case of KOH, the Ω value is smaller for KQF than for KQ, suggesting that the occurrence of feldspar somehow diminishes the efficacy of KOH as an amorphous phase booster, while for NaOH the Ω values are very similar for KQ and KQF, suggesting that the presence of feldspar has no influence on the production of the amorphous phase.
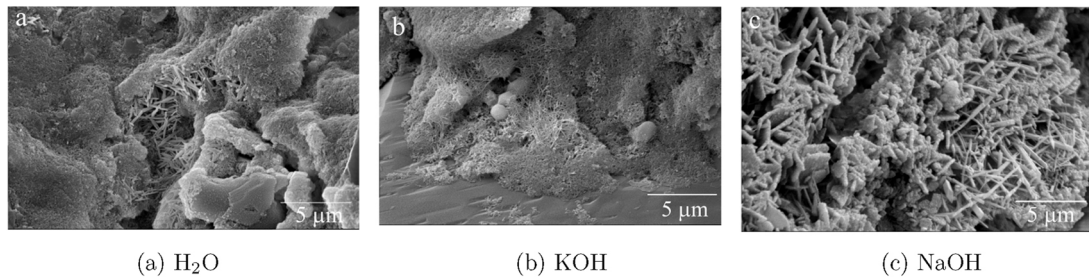
(a) H$_2$O   (b) KOH   (c) NaOH

Fig. 8. Secondary electron images of KQ-samples and different mineralisers. Q4 is used.
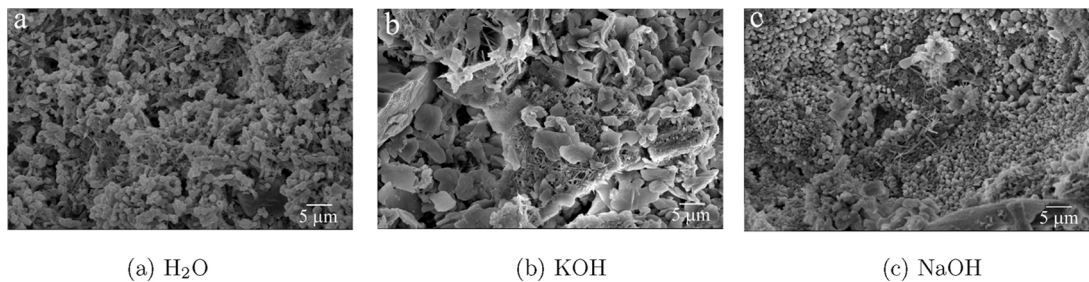

(a) H$_2$O   (b) KOH   (c) NaOH

Fig. 9. Secondary electron images of KQF-samples and different mineralisers. Q4 is used.

- influence on the crystalline phases: $\Omega_{NaOH,quartz} < \Omega_{NaOH,mullite}$, in KQ, whereas the reverse occurs in KQF, so NaOH produces a smaller amount of mullite in presence of feldspar, than with only kaolinite and quartz. The opposite happens for KOH.

5. Conclusions

The use of NaOH and KOH as mineralisers has been demonstrated to be effective to tailor the amount of amorphous phase in the final ceramic product, by affecting the fundamental equilibrium reaction between crystalline (quartz and mullite) and amorphous phases. In particular:

- Both NaOH and KOH shift the crystalline-*versus*-amorphous phases reaction towards an amorphous phase. However, their coefficients, in the calculation of the Gibbs energy of formation of the amorphous phase, have different absolute values, thus suggesting that either mineraliser affects the fundamental reactions in its own way. The difference between the two mineralisers is more marked in KQF, which thing indicates that the presence of feldspar helps diversifying the action of NaOH *versus* KOH;
- the size-dependent-coefficients are significantly smaller than those of the mineralisers, in absolute value, demonstrating that the effect due to quartz particle size is modest with respect to the one of the mineralisers. The size-dependent-coefficients have opposite sign in KQ and KQF, thus suggesting that an increase of *s* shifts the fundamental reaction towards the amorphous component, in kaolinite + quartz system, and towards the crystal phases, in kaolinite + quartz + feldspar system;
- the presence of feldspar does influence the final phase formation process. In KQF, Q4 yields amorphous phase contents over 90 wt%, with NaOH. In KQ, Q28 allows one to obtain amorphous material up to 90 wt%, using both KOH and NaOH. In general, the trend of the phase-contents *versus* mineraliser amount tends to show a decrease of crystalline phase in favour of glass upon increasing KOH/NaOH. A high level of irregularity is observable in the case of the relationship between phase-contents and quartz particle size. We think this is reflective of SiO$_2$ having a relevant role in the process. In fact, even comparatively small changes of its content

as a constituent of the amorphous phase impact heavily upon the equilibrium and, as a consequence, the phases that stabilise;
- The efficiencies (Ω) of NaOH and KOH reveal that they are boosters of amorphous phase (*i.e.* $\Omega_{NaOH/KOH,amorph} > 0$), at the expenses of crystalline phases (*i.e.* $\Omega_{NaOH/KOH,mullite/quartz} < 0$). This might be related to a tendency of Na$^+$ and K$^+$ to enter cages of the SiO$_2$-Al$_2$O$_3$ amorphous phase and to act as network modifiers that impair long range ordering. However, taking into account the absolute Ω-values, NaOH results in a more efficient promoter of amorphous phase than KOH;
- the amount of secondary mullite in the final products is favoured by the presence of feldspar. Quartz particle size does not influence the secondary mullite morphology, neither in KQ nor in KQF. In the KQ-system, NaOH boosts mullite length, whereas in the KQF-system such effect is promoted by KOH. This demonstrates that (i) mineralisers are able to influence textural aspects of relevance to mechanical properties in ceramics, and that (ii) the nature of a mineraliser plays a role that depends on the other slip's components, *i.e.* KQ- *versus* KQF-system.

The use of NaOH and KOH as mineralisers has been proven to be a realistic alternative to the fluxes that are traditionally used in the production of sanitary-ware. In particular, with respect to feldspars, they are strongly cost reducing, even though the change in pH of the slips needs to be counterbalanced. A possible reduction of the maximum temperature of the heating cycle can also be a by-product of this substitution, in conformity with the recent challenge of completely removing the fluxes from the starting ceramic mixture [10,11]. Their use in combination with feldspars can also be of some practical interest, as they tend (though in a different way for Na and K) to potentiate the effect on feldspars as fluxes (see Adamo et al. [3] for a comparison with Na-feldspar alone). With respect to recycled glasses [5–8], the use of NaOH and KOH has certainly the advantage of a strict compositional control, avoiding any possible issue due to the presence of extraneous elements, whose influence on the final product cannot be easily controlled or predicted [4]. Moreover, the amount of mineraliser and the final amorphous content can be easily related for different (and more complex) starting mixtures, making it easy to predict the final technological

properties (such as density, porosity, and so on) that depend on the amount of the amorphous phase.

Acknowledgements

References

[1] A. King, Ceramic Technology and Processing, William Andrew Publishing, 2001.

[2] W. Lee, Y. Iqbal, Influence of mixing on mullite formation in porcelain, J. Eur. Ceram. Soc. 21 (2001) 2583–2586.

[3] I. Adamo, V. Diella, A. Pavese, P. Vignola, F. Francescon, Na-feldspar (F) and kaolinite (K) system at high temperature: resulting phase composition, micro-structural features and mullite-glass Gibbs energy of formation, as a function of F/K ratio and kaolinite crystallinity, J. Eur. Ceram. Soc. 33 (2013) 3387–3395.

[4] V. Diella, I. Adamo, L. Pagliari, A. Pavese, F. Francescon, Effects of particle size distribution and starting phase composition in Na-feldspar/kaolinite system at high temperature, J. Eur. Ceram. Soc. 35 (2015) 1327–1335.

[5] N. Marinoni, D. D'Alessio, V. Diella, A. Pavese, F. Francescon, Effects of soda-lime-silica waste glass on mullite formation kinetics and micro-structures development in vitreous ceramics, J. Environ. Manag. 124 (2013) 100–107, doi:10.1016/j.jenvman.2013.02.048.

[6] E. Bernardo, G. Scarinci, P. Bertuzzi, P. Ercole, L. Ramon, Recycling of waste glasses into partially crystallised glass foam, J. Porous Mater. 17 (2010) 359–365.

[7] F. Matteucci, M. Dondi, G. Guarini, Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles, Ceram. Int. 28 (2002) 873–880.

[8] T. Tarvornpanich, G. Souza, W. Lee, Microstructural evolution on firing soda-lime-silica glass fluxed whitewares, J. Am. Ceram. Soc. 88 (2005) 1302–1308.

[9] A.M. Venezia, V.L. Parola, A. Longo, A. Martorana, Effect of alkali ions on the amorphous to crystalline phase transition of silica, J. Solid State Chem. 161 (2) (2001) 373–378.

[10] T. Ohji, M. Singh, Engineered Ceramics: Current Status and Future Products, Wiley, 2016.

[11] W. Holand, G. Beall, Glass-Ceramic Technology, Wiley, 2012.

[12] L. Pagliari, M. Dapiaggi, A. Pavese, F. Francescon, A kinetic study of the quartz-cristobalite phase transition, J. Eur. Ceram. Soc. 33 (2013) 3403–3410.

[13] M. Dapiaggi, L. Pagliari, A. Pavese, L. Sciascia, M. Merli, F. Francescon, The formation of silica high temperature polymorphs from quartz: Influence of grain size and mineralising agents, J. Eur. Ceram. Soc. 35 (2015) 4547–4555.

[14] A. Bernasconi, V. Diella, N. Marinoni, A. Pavese, F. Francescon, Influence of some industrially relevant properties of traditional sanitary-ware glaze, Ceram. Int. 38 (2012) 5859–5870.

[15] G. Stathis, A. Ekonomakou, C. Stournaras, C. Ftikos, Effect of firing conditions, filler grain size and quartz content on bending strength and physical properties of sanitary ware porcelain, J. Eur. Ceram. Soc. 24 (2004) 2357–2366.

[16] R. Rice, Porosity in Ceramics: Properties and Applications, Marcel Dekker Inc, 1998.

[17] C. Chen, G. Lan, W. Tuan, Microstructural evolution of mullite during the sintering of kaolin powder compacts, Ceram. Int. 26 (2000) 715–720.

[18] A. Pagani, F. Francescon, A. Pavese, V. Diella, Sanitary-ware vitreous body characterization method by optical microscopy, elemental maps, image processing and X-ray powder diffraction, J. Eur. Ceram. Soc. 30 (2010) 1267–1275.

[19] N. Marinoni, D. D'Alessio, V. Diella, A. Pavese, F. Francescon, Effects of soda-lime-silica waste glass on mullite formation kinetics and micro-structures development in vitreous ceramics, J. Environ. Manag. 124 (2013) 100–107, http://dx.doi.org/10.1016/j.jenvman.2013.02.048.

[20] A. Bernasconi, M. Dapiaggi, A.F. Gualtieri, Accuracy in quantitative phase analysis of mixtures with large amorphous contents. the case of zircon rich sanitary-ware glazes, J. Appl. Crystallogr. 47 (2014) 136–145.

[21] B.H. Toby, R.B. Von Dreele, GSAS-II: the genesis of a modern open-source all purpose crystallography software package, J. Appl. Crystallogr. 46 (2013) 544–549.

[22] H. Schneider, J.B.H. Schreuer, Structure and properties of mullite – a review, J. Eur. Ceram. Soc. 28 (2008) 329–344.

[23] Y. Iqbal, W. Lee, Microstructural evolution in triaxial porcelain, J. Am. Ceram. Soc. 83 (2000) 3121–3127.

[24] W. Lee, G. Souza, C.J.M. Tarvornpanich, T.Y. Iqbal, Mullite formation in clays and clay-derived vitreous ceramics, J. Eur. Ceram. Soc. 28 (2008) 46571.