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Using phase diagrams to deal with moisture expansion

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Abstract

Consensus has it that the post-fabrication moisture expansion of fired clay-based materials is governed by the presence of amorphous and/or vitreous phases. In this work, very simple calculations using the lever rule and the phase diagram of the Al_2O_3–SiO_2–K_2O (A–S–K) system, were used to show that the experimentally observed dependencies between moisture expansion and the A/S and K/A weight ratios in clay-based compositions can be correlated with the amount of liquid phase formed during the initial melting of the composition, which remains in the fired body as a vitreous phase. This correlation might, if judiciously used, help ceramists in the choice of additives and/or processing conditions, while avoiding changes in the firing temperatures. Also, the results obtained throw a sharper light in the dual and, in this respect, antagonistic role played by the liquid phase during firing.

Keywords: C. Lifetime (Moisture expansion); D. Traditional ceramics; E. Structural applications

1. Introduction

The irreversible expansion of fired clay-based materials under natural climatic conditions, as they interact with ambient moisture, is a spontaneous process that starts as soon as the products are removed from the furnace and lasts for years. Moisture expansion can result not only in floor and wall tiles that become drummy or have pop-up failure, but also in mechanical weakening susceptible of causing catastrophic failure of the structure concerned. Product damage and destruction occur when the expansion is restrained and the stress build up exceeds the material elasticity limit. Together with salt attack, moisture expansion is the most common cause of decay of brick masonry and wall and roofing tiles all over the world.

Moisture expansion first caught the attention of ceramists in the late 1920s [1,2]. As a result, standards were introduced to experimentally determine and specify limits to the acceptable moisture expansion of ceramic materials, particularly those used in civil construction (moisture expansion of glazed ceramic tiles results in crazing, rather than structural damage, and there are specific standards to evaluate the crazing resistance of glazed tiles).

In recent decades, the changes in the manufacture processes and prompt delivery to the building site, the adopted civil construction techniques and the architectural dictates (e.g. demand for light coloured façade bricks), have contributed to the resurgence of interest in moisture expansion and its consequences [3–6].

The determination of the characteristic expansion of bricks fresh from the kiln, i.e. the prediction of what their natural unrestrained moisture expansion will be after a 5-year period, needed to appropriately design the spacing and widths of the gaps necessary to accommodate the differential movements within a building, is but one of the reasons to study this phenomenon [7–9].

Related to this, the need arose to design a post-mortem test method capable of estimating the moisture expansion already experienced by aged materials. Moisture expansion has taken the blame for the catastrophic failure of several structures and such unpredictable accidents often lead to legal suits that require expert forensic advice.

Also, given that moisture expansion is a time-dependent phenomenon, ceramic products become more

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susceptible as they age. This may present significant problems in accreditation procedures. In fact a product may receive accreditation as having fulfilled the standard requirements but, if the product has marginal approval straight after manufacture, later on it might become incapable of passing the same test.

From the above it follows that ceramists had to embark in fundamental studies [10–13] seeking an understanding of the likely causes of moisture expansion, the influence of various factors on the kinetics and extent of the expansion, and the correlation with the relief of thermal stresses and externally applied loads, to be able to adapt the manufacture process accordingly.

2. State of the art

The mechanisms by which a ceramic body expands when exposed to water vapour were first set out in the mid 1950s and are based on the reduction of internal surface energy caused by the dissociative chemisorption of water molecules [14–18]. Water adsorbed on the surface of a body reduces its surface energy and, as the internal compression is relieved, the body behaves elastically and expands. The magnitude of the expansion will depend on the magnitude of the surface energy reduction and also on the bulk modulus of elasticity of the body. Surfaces that have a large number of unsatisfied valency bonds will undergo a large reduction in surface energy. Crystalline materials generally have relatively low surface energies and therefore are essentially inert to moisture whereas amorphous materials, namely amorphous silicates, are likely to have high surface energies. Both the fracture toughness and the modulus of elasticity might decrease with increasing moisture expansion [19], which explains the weakening in mechanical strength that accompanies moisture expansion.

Moisture expansion was found to be related with the available surface area (i.e. pores, channels and cracks near exposed surfaces), and essentially dependent on the chemical composition of the amorphous phase and its relative content (thus, the mineralogical composition of the raw materials and firing temperature and time).

Most research work aimed at establishing the influence of various factors on the kinetics and magnitude of moisture expansion has been concerned with clay-based compositions whose post-fabrication moisture expansion generally peaks when the firing temperature was in the range of 950–1050 °C. This temperature range includes the decomposition of kaolinite with the release of amorphous silica, the decomposition of carbonates with the release of highly water-reactive oxides (e.g. lime, magnesia) and the low melting eutectic temperatures in the relevant part of the multicomponent system. Thus, if the ceramic composition is not given enough time to mature at the correct firing temperature, the equilibrium-dictated reactions will not be complete and the resulting ceramic body will be prone to contain much porosity, a high content of unreacted amorphous and/or vitreous phases and, quite likely, residual water-reactive phases produced in the decomposition of added carbonates, that did not receive enough energy to combine with other constituents and transform into inert crystalline phases.

Since it has been established with a reasonable degree of confidence that the post-fabrication moisture expansion of fired clay-based materials is governed by the presence of amorphous and/or vitreous phases, an interpretation of the phenomenon can be sought in the phase equilibrium diagram of the appropriate system. The major chemical constituents of fired-clay bodies are alumina and silica and, among the minor constituents, alkaline oxides play a rather significant role as fluxes during the firing stage of the processing. Also, these constituents have been recognized to affect the moisture expansion and plots of moisture expansion versus the alumina/silica and alumina/alkalies weight ratios are commonly found in the relevant literature [17]. Among the alkalies, it is known that lithium oxide has a fluxing effect on the compositions stronger than that of sodium or potassium oxides and that the latter form more viscous liquid phases that show greater difficulty in crystallizing. These will most likely remain in the fired body as a vitreous phase. Thus, the systems Al_2O_3–SiO_2–K_2O and Al_2O_3–SiO_2–Na_2O will be better suited to investigate a possible correlation between moisture expansion and the amount of vitreous phase in the system. These two systems have rather similar phase diagrams and, given that K_2O leads to lower melting temperatures, the Al_2O_3–SiO_2–K_2O phase diagram can serve as a model system for an interpretation of the phenomenon.

It must be kept in mind that the liquid phase formed during firing also controls sintering and densification. The phase diagram, being based on thermodynamics, does not account for the kinetics of the on-going reactions and any attempt to reduce the amount of that liquid phase, aimed at reducing moisture expansion, will most likely entail, in the fired body, a further departure from equilibrium, with increased porosity and the corresponding poorer mechanical strength. Additives used to reduce the amount of liquid might also bring about extra difficulties in green processing. Thus, even if moisture expansion would be expected to decrease as a result of the reduced amount of vitreous phase, it might end up increasing, given the increase in available exposed surface area.

3. Results and discussion

The following discussion is conducted in terms of liquid contents formed when the system begins to melt.

Although, in industrial practice, firing temperatures normally exceed this first-melting temperature, the reactions in the alumino–silicate systems are quite sluggish and some phases, notably quartz, fail to dissolve up to the saturation limit of that liquid phase. Also, the observed trends for first-melting remain very much valid for higher temperatures and systems with more components. In this way, the conclusions extracted from the phase diagram of the Al_2O_3–SiO_2–K_2O (A–S–K) system, can be used as rule of thumb when dealing with practical systems, with more components, higher firing temperatures and non-equilibrium processes.

In the A–S–K system, all common clays belong to the sub-system mullite–silica–feldspar (A_3S_2–S–KAS_6) in which first-melting occurs at the eutectic point at 985 °C. The liquid phase formed at this eutectic point is in equilibrium with, and is related by a tie-triangle to, two solid phases, either A_3S_2 and silica, or A_3S_2 and KAS_6, depending on the K_2O content and the A/S ratio of the mixture (Fig. 1).

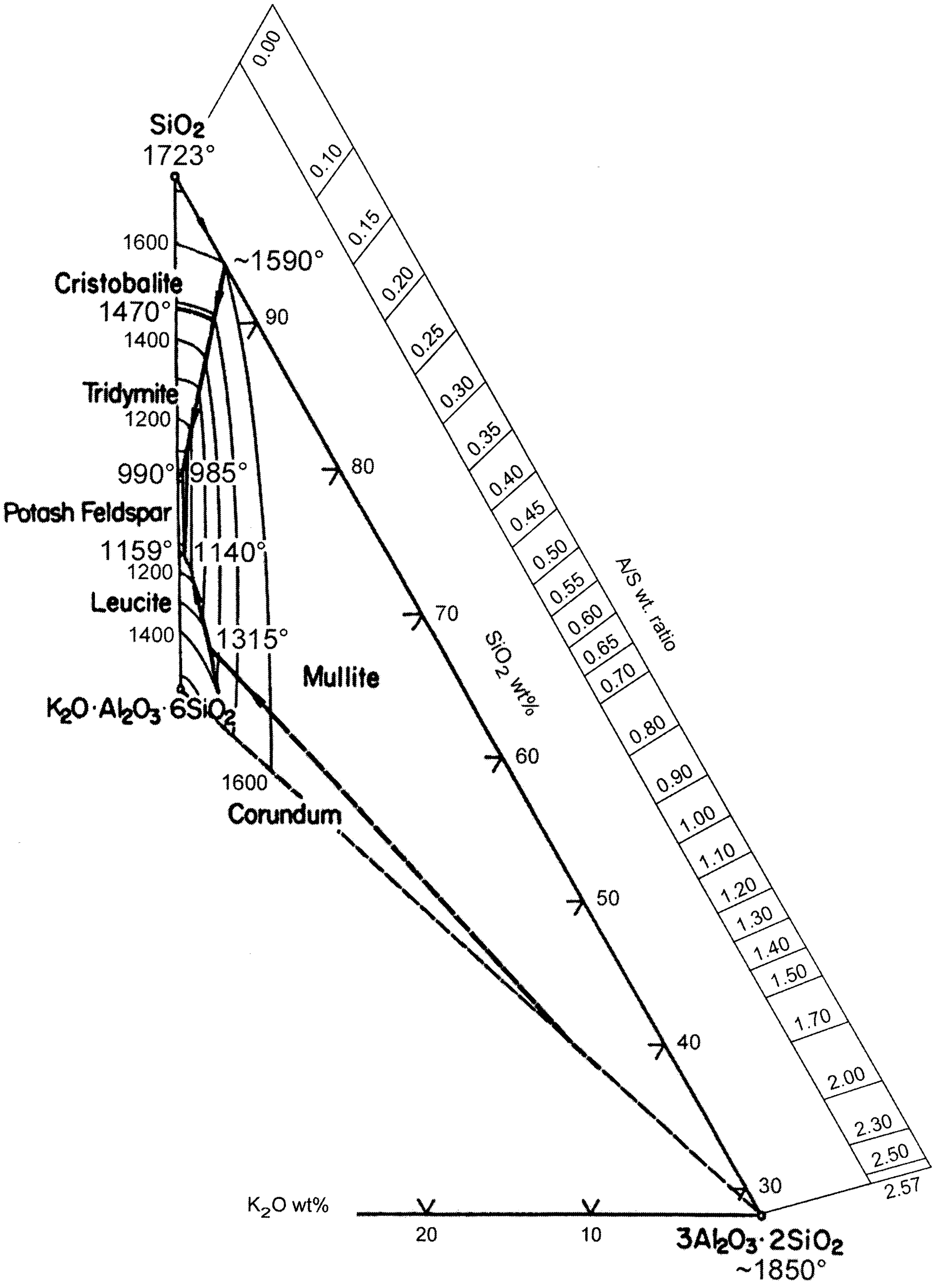

Fig. 1. Phase diagram of the sub-system mullite–silica–feldspar (A_3S_2–S–KAS_6), used to investigate a possible correlation between moisture expansion and the amount of vitreous phase. All common clays belong to this part of the Al_2O_3–SiO_2–K_2O system.

As an aside, it should be noted that the composition range of interest here, even in the more refractory systems Al_2O_3–SiO_2–CaO (A–S–C) and Al_2O_3–SiO_2–MgO (A–S–M), is also morphologically similar to that in the A–S–K system (limestone, dolomite, magnesite and talc are common additives [20] used to, among other things, try to reduce moisture expansion and glaze crazing), and the same reasoning, as described later, could be applied with the appropriate changes of sub-systems (viz. A_3S_2–S–CAS_2 and A_3S_2–S–$M_2A_2S_5$) and initial melting temperatures (1345 and 1440 °C, respectively).

For low K_2O contents (~1 to 4 wt.%) and low A/S ratios (such as in kaolinite (A/S = 0.85) or lower), the first-melting tie-triangle has apexes on the 985 °C eutectic liquid, mullite and silica (Fig. 1). It so happens that constant K_2O content lines are parallel to the A_3S_2–S side of the tie-triangle, opposite the liquid apex. From triangles geometry it follows that the amount of liquid formed, calculated using the lever rule, is constant for each constant K_2O content, whatever the value of the A/S ratio. This behaviour extends to fairly high K_2O contents (~9 wt.%) when the A/S ratio is appropriately low ($A/S < 0.14$), the amount of liquid reaching up to complete melting at 985 °C.

As the A/S ratio increases, increasing K_2O contents eventually lead the compositions across the A_3S_2–liquid tie-line and into the other first-melting tie-triangle (viz. 985 °C eutectic liquid, mullite and feldspar) within which the amount of liquid formed depends both on the K_2O content and the A/S ratio of the mixture. Compositions with 10 wt.% K_2O or more lie in this second first-melting tie-triangle (Fig. 1).

Fig. 2 illustrates the two situations, in terms of constant K_2O content contours, and is constructed so that it can be compared with the experimental plots of A/S ratio vs. moisture expansion found in the literature [17]. The first-liquid line for the pure A_3S_2–S system is also represented, clearly showing the fluxing effect of the added alkali-oxide. The area in between the two solid grey lines corresponds to the composition range in which the amount of first-liquid is independent of the A/S ratio (*viz.* within the liquid-A_3S_2–S first-melting tie-triangle).

Fig. 3 shows the relationship between the alkali-oxide/alumina weight ratio and the amount of first-liquid and, again, is constructed so that it can be compared with the experimental plots of K/A ratio vs. moisture expansion found in the literature [17].

Most experimental results published and plotted in that way, are concerned with a particular clay-based composition to which various additions are made. A lot of scattering is observed but, still, a common trend can be identified: moisture expansion tends to increase with increasing K/A ratio and decreasing A/S ratio.

The experimentally observed trend between the A/S and K/A ratios and moisture expansion noticeably correlates with the A/S and K/A vs.% liquid (Figs. 2 and 3) for compositions lying within the second first-melting tie-triangle (viz. the liquid–mullite–feldspar). In terms of the theoretical data extracted from the phase diagram, a

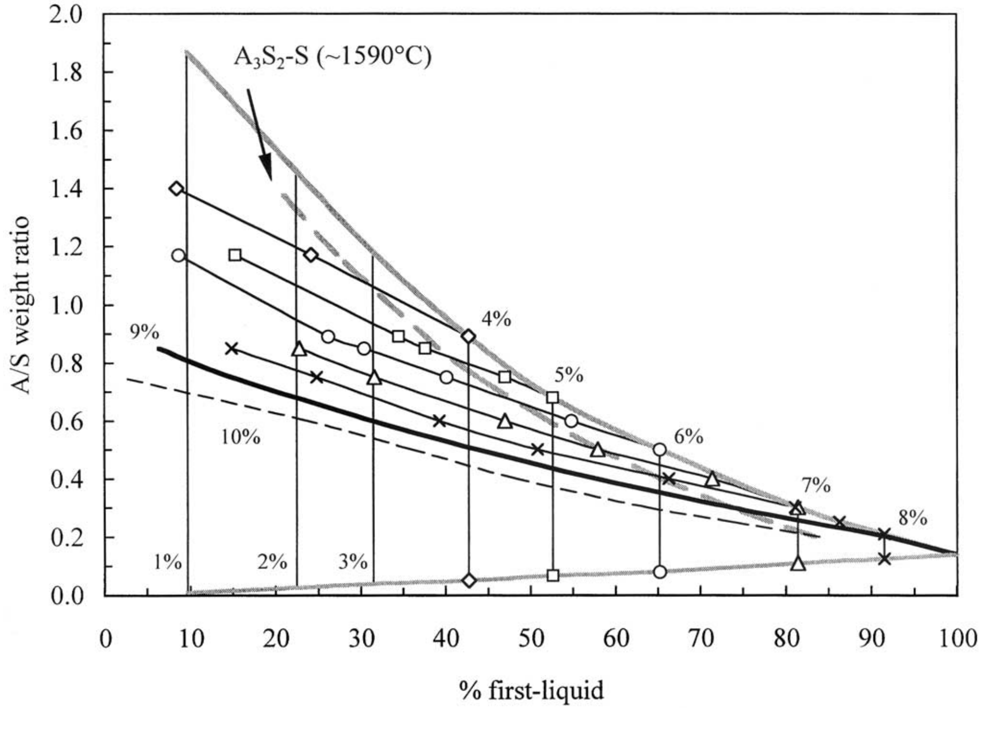

Fig. 2. Correlation between the alumina/silica weight ratio and the amount of liquid phase formed during initial melting (985 °C), as a function of K_2O content. The thick dashed grey line represents initial melting (~1590 °C) in the A_3S_2–S binary system.

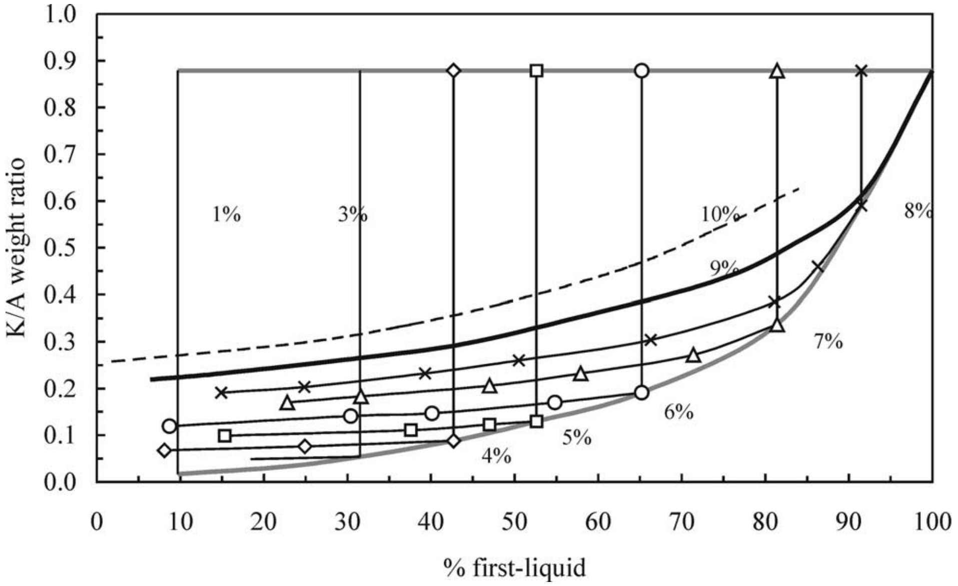

Fig. 3. Correlation between the K_2O/alumina weight ratio and the amount of liquid phase formed during initial melting (985 °C), as a function of K_2O content.

very close polynomial dependence between the amount of first-liquid and the A/S and K/A ratios can be observed for compositions belonging to the liquid–A_3S_2–KAS_6 tie-triangle, scatter being eliminated when data points are plotted as constant K_2O content contours.

What has been overlooked so far is the composition range within which the amount of first-liquid is independent of both the A/S and K/A ratios and a function solely of the K_2O content (i.e. the liquid–A_3S_2–S tie-triangle). If moisture expansion did indeed depend on the amount of the liquid (vitreous) phase present, this composition range could be either the one to look for, since it provides a rather forgiving composition range for the same amount of liquid produced, or the one to avoid, if the amount of liquid is already too high. Authors are seldom aware of the implications of the movement of the composition within the system phase diagram while seeking an indiscriminate correlation among all data points.

Indeed, it is most interesting to note that, for a given A/S ratio and increasing K_2O contents, the amount of first-liquid increases while the composition remains within the first tie-triangle, but starts decreasing when the composition crosses the boundary tie-line liquid–A_3S_2. As an example, for kaolinite (A/S = 0.85), 1% K_2O leads to ~10% liquid at 895 °C and the amount of liquid steadily increases to ~46% when the K_2O content reaches ~4.3%; from this point onwards, further increments in the K_2O content actually lead to a decrease in the amount of liquid formed at first-melting. This can be better observed in Fig. 4, which is merely a rearrangement of the data in Fig. 2. The liquid maximum in each A/S contour represents, in the phase diagram, the intersection of the particular A/S line with the liquid–A_3S_2 tie-line. Contours with increasing A/S values show a lower liquid maximum at successively lower K_2O contents.

The same trends would be found if a different (higher) temperature was chosen. The calculated liquid phase contents would be higher, but the shape of the curves would be similar.

The practical implications of Fig. 4 are obvious: without changing the firing temperature, to decrease the amount of liquid formed, the K_2O content could be increased beyond the maximum in the particular A/S contour or the alumina content could be increased in order to move to a higher A/S contour (and hence a lower K/A ratio), with a lower liquid maximum. For high A/S ratios, changes in the K_2O content have little effect on the K/A ratio and it might be easy to increase the K_2O content and push the composition across the liquid–A_3S_2 tie-line. For low A/S ratios, the maximum in the contour is already high and not easily over taken. Any increase in the K_2O content translates into a sharp increase in the K/A ratio, accompanied by an equally sharp increase in the amount of first-liquid. In this case, moving to a higher A/S contour might be a better alternative.

Common clays, on average, have A/S ratios below 0.4 and an overall alkali content of 2–4%. These compositions lie in the broadest part of the liquid–A_3S_2–S tie-triangle and Fig. 4 shows that, for this level of K_2O, it is practically irrelevant what the value of the A/S ratio is. The amount of vitreous phase formed will always be high and dependent only on the K_2O content. It will not be easy to decrease the amount of that liquid phase. However, for this composition range the role played by

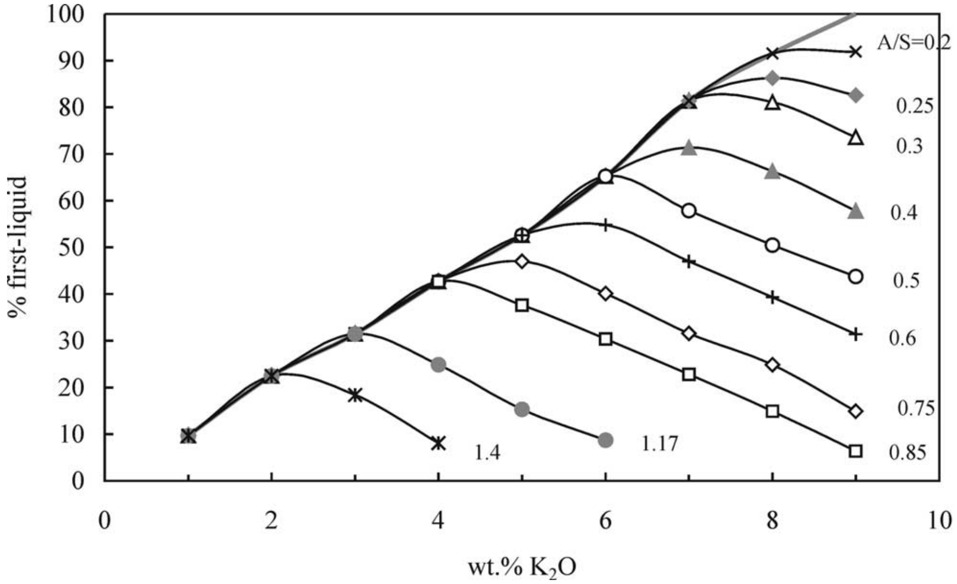

Fig. 4. Correlation between the amount of liquid phase formed during initial melting and the K_2O content, as a function of the alumina/silica weight ratio. The thick grey line corresponds to a 0.14 A/S weight ratio.

that liquid phase during firing might be far more important than the role of the resultant vitreous phase during the post-fired service life of the ceramic. In this case, the densification effect of the liquid phase, which, for a given composition, greatly depends on the microstructure, might override the susceptibility of the corresponding residual vitreous phase to moisture, which would be the same for all compositions with the same K_2O content. A study [21] carried out with several commercial single-fired (ca. 30 min) red-clay tiles of unspecified processing, with A/S ratios between 0.26 and 0.38 and alkali oxide contents below 4%, showed that the usual trends between moisture expansion and the A/S and (K + N)/A weight ratios are not observed, nor does moisture expansion depend only on the K_2O content. This study showed how the liquid phase formed during firing first controls densification and then affects moisture expansion. A reduction in its amount does not necessarily reduce moisture expansion, as it hinders densification with the consequent increase in porosity (hence, in water absorption).

The reasoning in terms of K/A ratio and varying K_2O content is a little trickier, since one affects the other. For instance, when discussing the changes in the amount of liquid phase for a given K/A ratio, one must bear in mind that, to keep that K/A ratio constant, if the K_2O content is increased (or decreased), the A/S ratio must also be increased (or decreased). In the phase diagram, for both ratios, the composition moves along lines that go through one of the apexes but, while for the A/S ratio vs. liquid phase relationship, a constant A/S ratio and increasing K_2O content are represented by the same line, going through the K_2O apex, for the K/A ratio vs. liquid phase relationship the equivalent lines go through different apexes, i.e. the constant K/A line goes through the SiO_2 apex and the increasing K_2O content line goes through the K_2O apex.

Thus, it all comes up to a compromise between the A/S and K/A ratios, as they define a geometrical locus that separates the regions in which the amount of first-liquid depends only, and not only, on the K_2O content, corresponding to the two first-melting tie-triangles. Fig. 5 is constructed from data in Figs. 2 and 3 and illustrates the earlier discussion. The solid grey line is the boundary between the two regions and corresponds to the liquid phase maxima (again, these are points on the liquid–A_3S_2 tie-line in the phase diagram). To decrease the amount of vitreous phase, the composition has to be moved as far away as possible from that boundary line. If the A/S and K/A ratios place the composition in the left side region, the appropriate additive, within the A–S–K system, will be one that lowers the K_2O content; if the A/S and K/A ratios place the composition in the right side region, the appropriate additive will be one that raises the K_2O content.

Additions made in this light (e.g. more refractory clays, bauxite, silimanite or andalusite) might prove to yield better results, or at least more predictable results, in reducing moisture expansion than the more common additions of carbonates (e.g. limestone, dolomite, magnesite) or talc. The introduction of reactive oxides, such as produced during the decomposition of carbonates, will help reducing the amount of amorphous phases, notably silica, but might enhance the production of liquid at the firing temperature. With the addition of alien fluxes, first-melting will occur at lower temperatures in the quaternary (or higher order) system, the amount of liquid formed at the same firing temperature

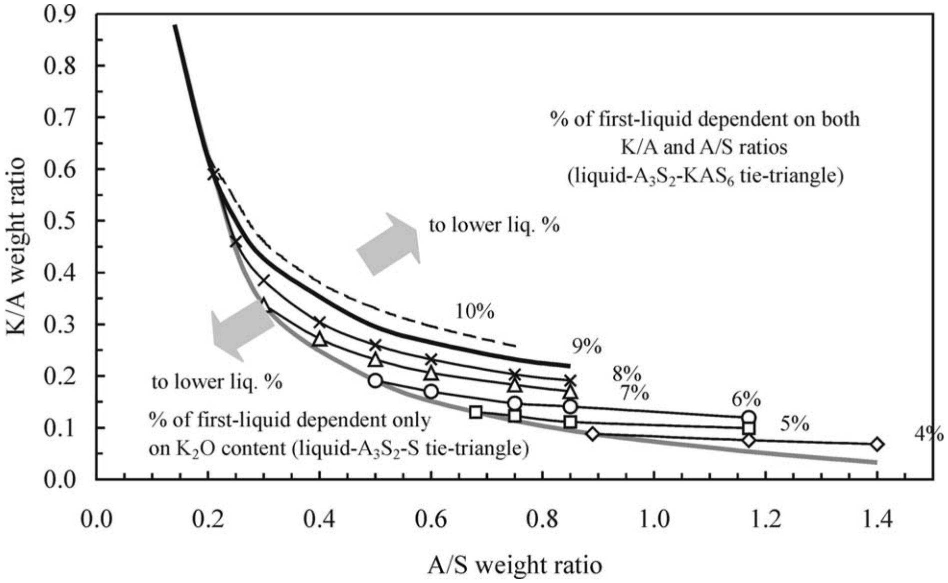

Fig. 5. Correlation between the A/S and K/A ratios, illustrating the geometrical locus that separates the regions in which the amount of first-liquid depends only, and not only, on the K_2O content, corresponding to the two relevant first-melting tie-triangles.

will likely be higher and it is the quality of that liquid phase, particularly its viscosity and wetting capability, that will determine its contribution to the densification process.

Additions of kaolin, refractory clays or andalusite (A/S ~ 0.70 and alkali content < 1%) contribute to increase the A/S ratio and might help in reducing the amount of vitreous phase. Although the resulting composition remains in the liquid–A_3S_2–S tie-triangle, the resulting K_2O content might be significantly reduced (see Fig. 2). The addition of a bauxite-type raw material, on the other hand, can be used to successfully bring the composition outside of that first-melting tie-triangle, raising the A/S ratio enough without much change in the K_2O content, with the corresponding decrease in the amount of vitreous phase.

On the other hand, additions of feldspar will increase the K_2O content but further decrease the A/S ratio. The raise in K_2O content is not beneficial since the liquid maximum in the new A/S contour that needs to be overtaken also moves to both higher values and K_2O contents (see Fig. 4).

4. Conclusions

Very simple calculations using the lever rule and the phase diagram of the Al_2O_3–SiO_2–K_2O (A–S–K) system showed that the experimentally observed dependencies between moisture expansion and the A/S and K/A weight ratios in clay-based compositions can be correlated with the amount of liquid phase formed during the initial melting of the composition, which remains in the fired body as a vitreous phase.

The geometrical layout of the diagram leads to the separation of compositions in two groups with rather dissimilar first-melting behaviours. Although they all start melting at the same temperature, they are tied by two different tie-triangles: in the liquid–A_3S_2–S tie-triangle the amount of first-liquid depends only on the K_2O content and increases sharply with it; in the liquid–A_3S_2–KAS_6 tie-triangle, on the contrary, the amount of first-liquid depends on the exact location of the composition (i.e. its A/S and K/A ratios) and, for a constant A/S ratio, it does actually decrease when the K_2O content increases.

This reasoning might sound all very simple for those who are well versed in the handling of phase diagrams but, for those who are not, they can also be translated into more familiar representations, hopefully easier to handle, such as Figs. 4 and 5. With only two independent variables (e.g. A/S ratio and K_2O content) it can become extremely simple to make an educated choice of additives, remaining in the A–S–K so that firing temperatures do not have to be raised.

It must be kept in mind that the liquid phase formed during firing also controls sintering and densification. Thus, any attempt to reduce the amount of that liquid phase will most likely entail a worse densification (hence, more porosity and exposed surface) and the fired body will consequently exhibit a poorer mechanical strength.

Also, some leeway must be given to the earlier results, to accommodate the presence of other minor constituents and added alien fluxes. Their presence might significantly alter, if not the general trends, at least the amount of first-liquid formed, and the initial melting temperature in the overall system will obviously be lower. In the end, moisture expansion might be reduced not because there is less vitreous phase but because the ceramic body is better densified and there is less porosity.

Acknowledgements

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