STUDY OF VITRIFICATION OF TILE BODIES WITHOUT AND WITH SPODUMENE

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INTRODUCTION

Homogeneous Vitrified Tiles, better known as Gres Porcellanato, have gained vast popularity in recent years. This, primarily is due to their excellant mechanical and technical qualities, i.e. low water absorption, high wear resistance, high breaking strength, high compressive strength, and ability to withstand chemical attack and frost. These tiles are normally fast fired in roller hearth kilns up to a peak temperature of about 1220°C at a cycle of about 60 minutes. The production of these bodies depend considerably on the combination of the properties of the raw materials used and the technology employed in the production processes to ensure and maintain a consistently high product quality. The world-wide increase in demand for these tiles has prompted considerable research studies into the use of new raw materials, improvements in the manufacturing processes, their physico-mechanical properties and the aesthetic qualities of the product. This research paper studies the vitrification of these tile bodies with and without spodumene.

Studies at Staffordshire University have shown that, at 900°C, there is perceptable melting in the matrix of the body, shown by detection of meniscus curves where platy grains in the matrix touch, and by the start of firing shrinkage. At these temperatures, feldspar grains are unmelted, so their alkali is locked within the crystal structure and is not available to diffuse into the matrix to contribute to melting there. It is thought that this starts at about 1100°C.

Meanwhile, as the temperature rises, there is evidence of increasing melting throughout the matrix, modifying the particle shapes and the porosity, and providing increasing firing shrinkage and reducing water absorption. It is mostly illite in clays which provides this melting. Contribution of alkali from feldspar to the matrix is shown by growth of mullite needles in the pools of liquid (glass after cooling) produced in the feldspar grains. As alkali diffuses away, the liquid composition reaches the field of primary crystallisation of mullite and more diffusion leads to more mullite formation. This is generally associated with higher temperatures and longer times spent over about 1100°C.

Acceptance of alkaline ions into the matrix will be faster when there is more liquid present in the matrix. This model is a simple one, complicated by feldspar relicts in vitrous bodies, some of which do, while others do not, contain mullite. This may reflect faster diffusion of (smaller) sodium than potassium ions. The importance of diffusion is consistent with well established effects of feldspar compositions, amounts and particle size ranges in classical ceramic bodies.

The present study involved comparing vitrified tile bodies without and with spodumene ($LiAlSiO_6$) as a supplementary flux. In this study, the control body of a typical Malaysian vitrified tile contains more soda than potash feldspar, and also contains pottery stones which are essentially mixtures of fine quartz and sericite. As spodumene encourages vitrification, there is considerable potential for a reduction in firing temperature. More interestingly is the reduction in the fired shrinkage giving the possibility of a product with a high level of sintering without a corresponding large dimensional variation.

EXPERIMENTAL

Laboratory scale trials were first carried out to investigate the different body mixes and the effects of different fineness of grinding of spodumene. Two different body formulae with spodumene, SPP01 and SPP03 were tested and compared against a control, which is a typical South East Asian vitrified body, coded as M3. The raw materials were ground in the usual way to obtain the required particle size. The body slips were then dried and made into test pieces. The pieces were pressed at a specific pressure of 400 kg/cm^2 in a laboratory hydraulic press. The samples were fired in an electric mufffle kiln at peak temperatures of 1130°, 1150°, 1170° and 1190°C.

The water absorption and fired shrinkage were then determined. Graph 1 shows the vitrification curve for the three bodies. The effects of spodumene in the SPP01 and SPP03 bodies clearly shows the potential for a reduction in the peak firing temperature.

The bodies were examined initially using reflected light to investigate porosity, using polished sections. These images distinguished only between holes (pores) and solid body and offers no information on the crystalline and glassy phases in the bodies. This information was available with Scanning Electron Microscopical (SEM) images which provide greater resolutions. The specimens were polished and etched using 4% hydrofluoric acid for 90 to 120 seconds to attack the glass phase to develop topography between crystals and glass giving constrast in the SEM images.

MICROSCOPICAL RESULTS AND DISCUSSION

Significant features include:-

(i) the development of solution rims round quartz grains. These are of the order of 1 μm wide and the width increases with increasing firing times and temperatures, and increasing melting of matrix surrounding them. It gives an indication of the effects of firing.

(ii) the development of mullite needles in feldspar relicts. Again, there is a general increase in development of these in feldspar relicts with longer times and

higher temperatures, and differences which are attributed to soda or potash feldspar. It is thought, but has not yet been comfirmed, that there is greater development within soda than potash feldspar relicts.

(iii) a similar development in spodumene relicts, with much greater development, in a given firing, in spodumene than in feldspar. This is taken to indicate greater diffusion of lithium out of the spodumene relicts than alkali from the feldspar relicts, and to explain the greater fluxing power of spodumene.

The potential difficulty of the high melting point of spodumene may be countered by the observation that, in these bodies, the spodumene is not on its own, as it is for melting point determinations, and heating rates are fast enough to prevent equilibrium conditions from being met. The evidence is clearly of melting of spodumene and diffusion of lithium out of the liquid, and reference may be made to Figure 1.

CONCLUSION

(i) spodumene, on its own, and particularly together with talc, is effective in reducing temperatures required to vitrify the tile bodies used in this study. These are typical of vitrified tile bodies made in South-East Asia, so the results have commercial potential.

(ii) the mechanism of fluxing using spodumene appears to be closely similar to that of feldspars, i.e., melting to liberate the alkaline ions and migration into the surrounding matrix to encourage melting and densification there.

The conventional variables of flux composition amount and particle size range seem to apply.

(iii) the evidence is, from mullite growth in relicts, that lithium is liberated in and diffuses out of spodumene relicts at lower temperatures than alkaline ions do from feldspar.

(iv) the microstructures of spodumene bodies resemble those of non-spodumene bodies which have been fired hotter, or longer, or both. There are no uncomfortably different microstructures.

(v) there are indications of improvements of strength and of depth of colour with spodumene incorporation in bodies. These, together with energy savings, counteract cost disadvantages of spodumene compared with feldspar fluxes.

(vi) there is evidence of feldspar surviving some commercial firings. This is to be expected in the largest grains in short firings. This indicates that conventional fluxing rules may not apply to today's faster firings.

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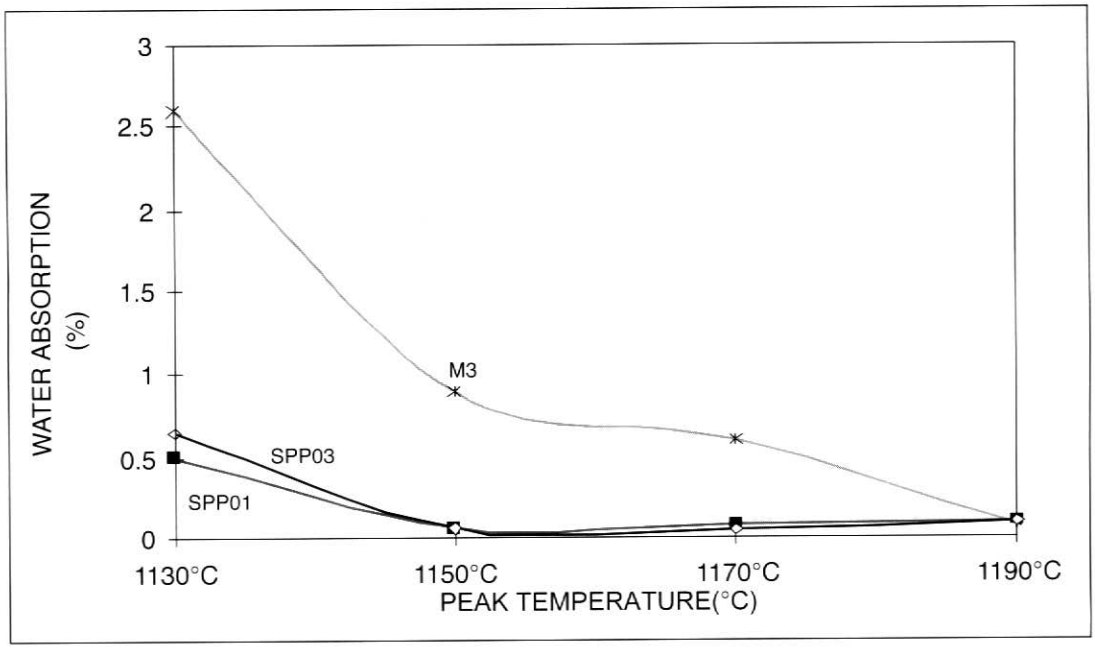

Graph 1. *Vitrification Curve Of Vitrified Tile Bodies With Water Absorption Vs Firing Temp.*

SPODUMENE AND FELDSPAR RELICTS

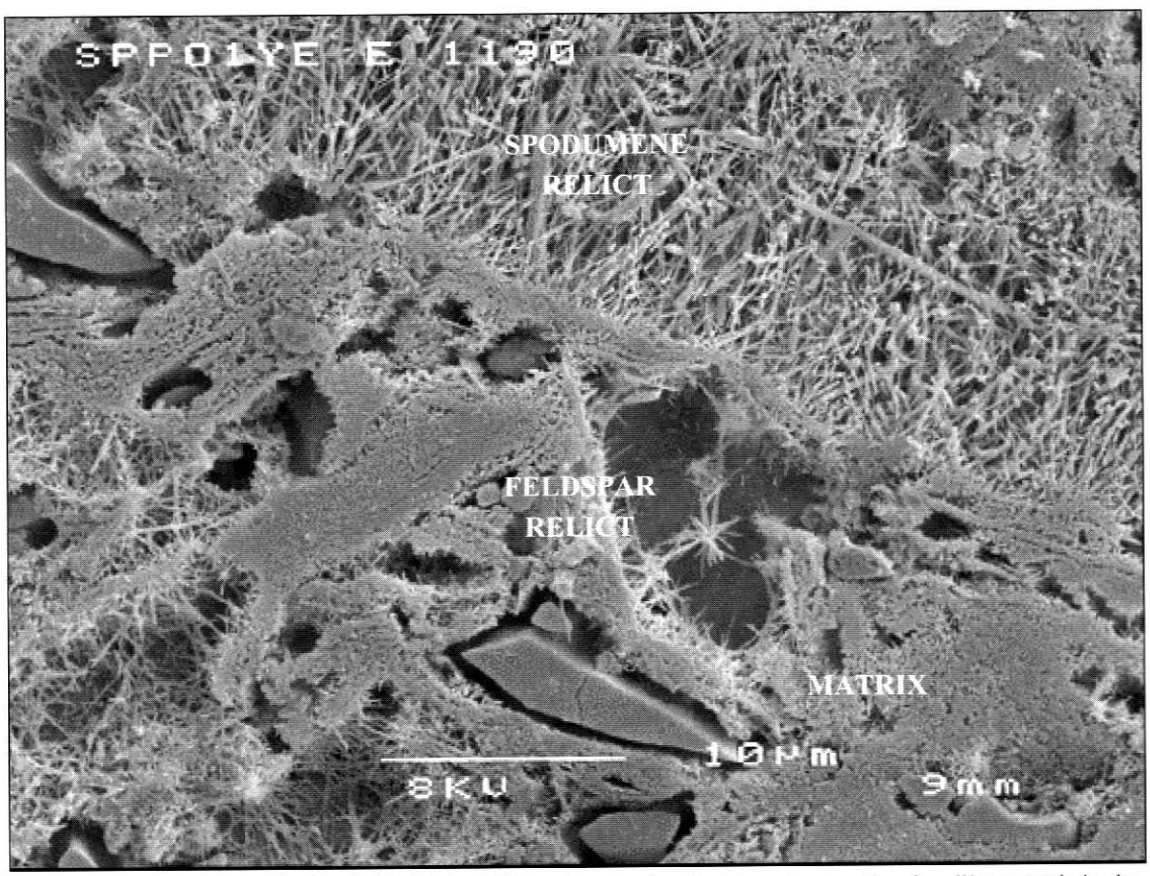

Figure 1. *SEM Micrograph of a vitrified body with spodumene showing a greater density of mullite crystals in the spodumene relict compared with the feldspar one.*

TYPICAL FEATURES OF VITRIFIED BODY

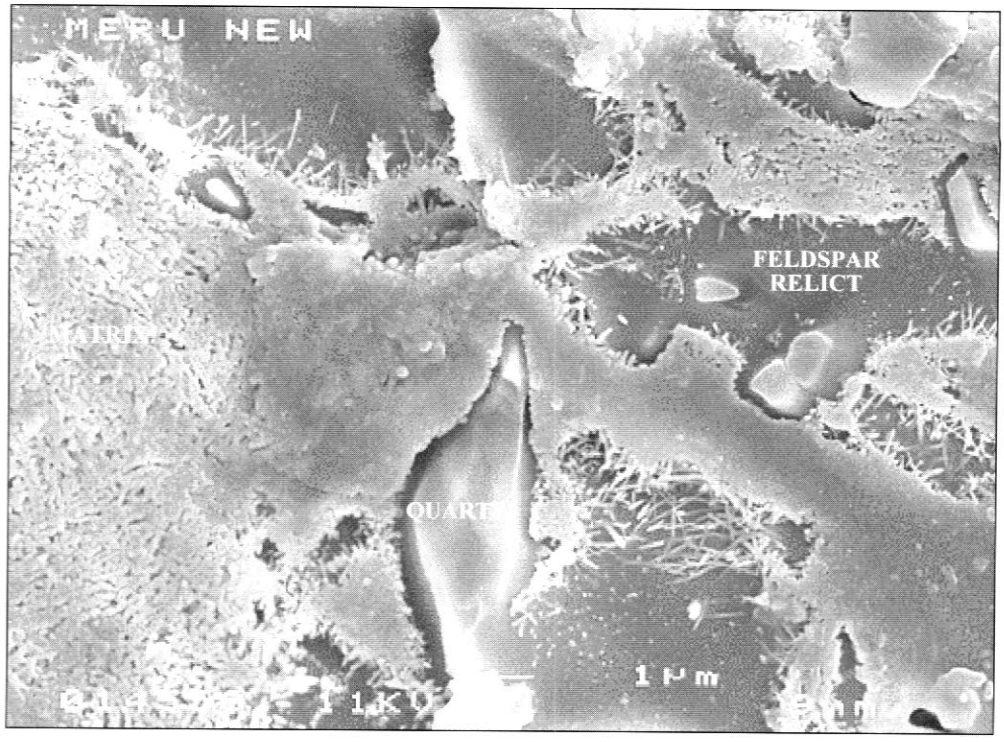

Figure 2. SEM Micropraph of the typical features of a vitrified body showing the quartz grain with its solution run, the pools of glass representing feldspar relicts and the dense matrix, mostly mullite (brighter arcas) with some glass (darker areas)

PORCELAIN BODY FIRED AT 900°C

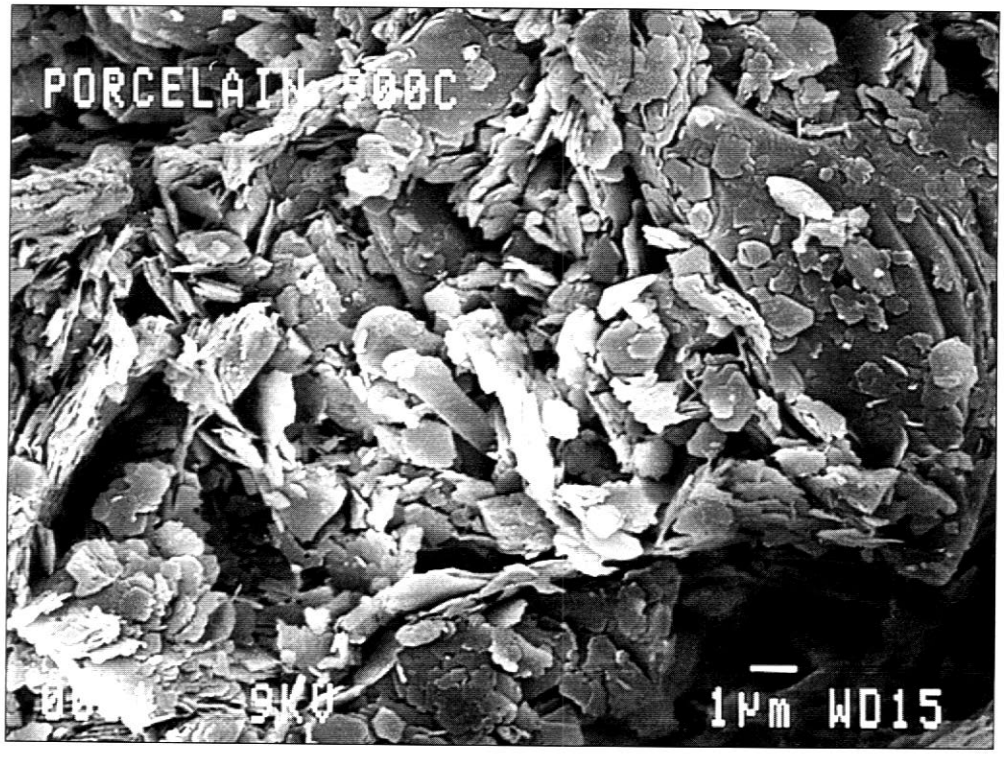

Figure 3. SEM Micrograph of a porcelain body fired at 900°C showing very little melting.

PORCELAIN BODY FIRED AT 1400°C

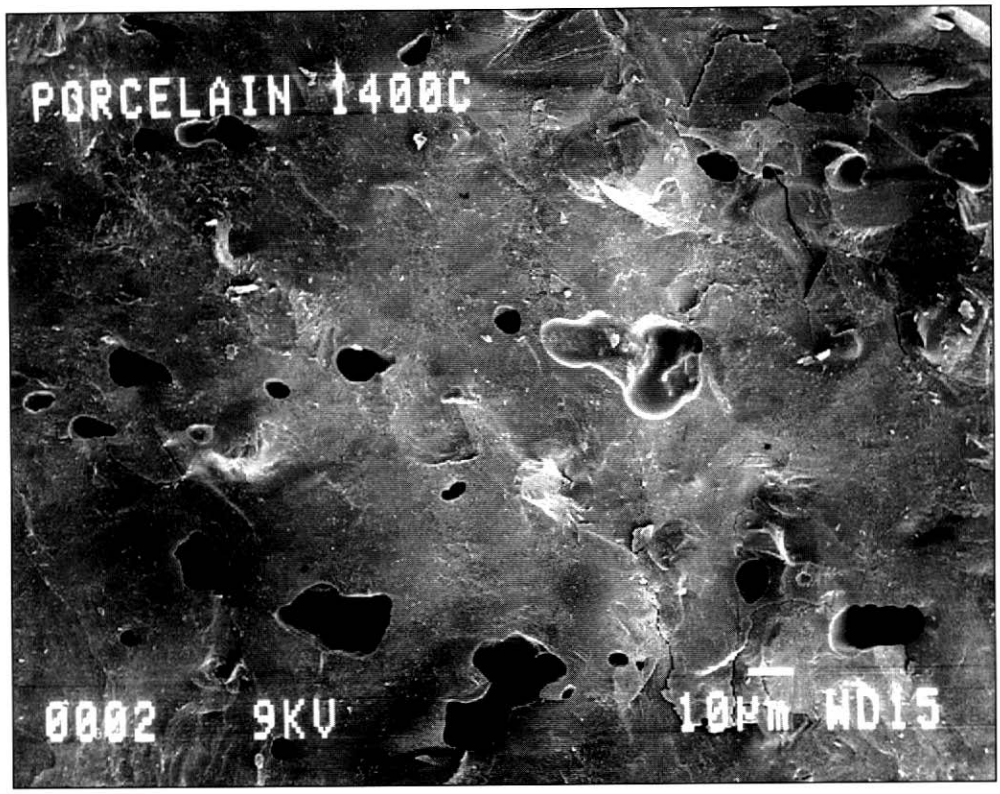

Figure 4. *SEM Micrograph of a porcelain body fired at 1400°C showing a high degree of vitrification.*