

Compaction pressure effects in the firing of self-vitrifying ceramic materials

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The firing behaviour of two self-vitrifying ceramic materials, coming from a magmatic rock of the aplite type consisting basically of quartz, feldspar and kaolin, both in the raw and purified (iron-free) state, were investigated as a function of the compacting pressure over the range 14 to 280 MN m⁻². The materials exhibit a linear relationship of firing shrinkage versus the logarithm of the cold compacting pressures in the temperature range where vitrification processes occur, while the linearity falls down outside this range. The iron oxide content lowers the vitrification temperature as well as the vitrification range. The observed linear relationship is quite similar to that exhibited by other self-vitrifying ceramic materials for wall and floor tiles previously investigated, and it does not seem to depend on the compacting characteristics of the powders. It has therefore to be related to the gradually growing glassy phases which arise during firing at increasing temperatures. This relationship may thus be considered as a general characteristic of the firing behaviour of strongly self-vitrifying ceramic materials when subjected to green density changes.

1. Introduction

In two previous papers [1, 2] the effects of the compaction pressure on the firing behaviour of Italian clays used for the production of wall and floor tiles (*maiolica*, *cottoforte* and red stoneware) were investigated. The densification behaviour exhibited a decrease of linear per cent firing shrinkage with the increase in compacting pressure in all cases, in spite of the difference in the composition of the raw materials. Furthermore, the linear per cent shrinkage was related by a linear relationship to the logarithm of the compaction pressure at firing temperature below those required for maximum densification. At higher temperature this behaviour strongly deviated from the straight line. The non-equilibrium processes occurring during firing are somewhat variable in these materials, depending on their composition. However, all lead to the formation of large amounts of glassy phases, increasing from *maiolica* to red stoneware, according to the raw materials composition and firing schedule [3-6]. In indus-

trial practice, such a simple relationship of shrinkage versus compaction pressure would be useful, if confirmed in a more general way, to predict the actual shrinkage of these ceramic materials during their manufacture. Therefore, the effect of cold compaction pressure on the firing shrinkage of a model self-vitrifying ceramic powder has been studied. This material, derived from an Elba rock, has been investigated previously with regard to its firing and overfiring behaviour at a constant forming pressure near that used in the industrial practice [7]. Such a multicomponent system exhibits a simpler composition than that of the clays actually used in the ceramic industry, but it has very similar vitrification behaviour. In practice, the cold compaction pressure cannot usually be changed over a large range, because of the general use of friction presses. However, similar changes in the green density of ceramic bodies can be obtained in other ways, such as by adding suitable binders and lubricants or changing the powder grain size distribution or shaping procedure.

2. Experimental

2.1. Materials

The materials investigated come from an Elba rock, available under the trade name of *Eurite*, which is basically a quartz-feldspar magmatic rock of the aplite type, and contains up to 23 wt% and more of kaolin. Two types of powder were investigated, the *Eurite* purified to remove iron oxide (RG) and the natural *Eurite* (N 250), where the iron oxide acts as a further fluxing agent. Their average compositions are shown in Table I. In the present study the powders were used in the same form as supplied to ceramic manufacturers, without being given any milling treatment. The powders were characterized by their grain size distribution and the so-called powder strength.

The grain size distribution was determined by both wet sieving and the Andreasen pipette

TABLE I Composition of purified and natural *Eurite* (wt %)

	RG	N 250
Loss on ignition	3.23	3.09
SiO ₂	75.03	73.80
Al ₂ O ₃	16.21	16.66
TiO ₂	0.17	0.18
Fe ₂ O ₃	negl.	1.10
CaO	0.32	0.46
MgO	0.40	0.40
K ₂ O	3.63	3.27
Na ₂ O	1.20	0.73
CaCO ₃	abs.	abs.

sedimentation technique, after stirring for 6 h in water to which sodium pyrophosphate had been added [8–10]. Fig. 1 shows that the grain size cumulative distributions are closely similar for both powders.

The powder strength is based on interpretation of compaction data plotted as the logarithm of pressure versus bulk density of the compacts [10, 11]. These were prepared by single-ended pressing in steel dies at pressures increasing from 0.06 to 280 MN m⁻², with an approximately constant rate of loading, using a hydraulic press. A rectangular die of cross-section 10 mm × 50 mm and a cylindrical die of 50 mm diameter were used. To minimize the effects of the die-wall friction, the height of the compacts were kept below 10 mm. To ensure that the compacts have sufficient strength to be handled, a small quantity of water (max 15 wt%) was added to the powders; this merely acts as a fugitive liquid in the subsequent firing [12, 13]. The total load applied to the compacts was measured on a previously calibrated Bourdon gauge. To determine their bulk density the dimensions were measured with a micrometer gauge to an accuracy of 0.02 mm. Fig. 2 shows the compaction data for the rectangular compacts. Similar behaviour was found for cylindrical compacts, except that their bulk densities were somewhat higher for the same compaction pressure, the differences probably arising from die-wall friction effects. Some ranges of linear behaviour can be seen, which may be

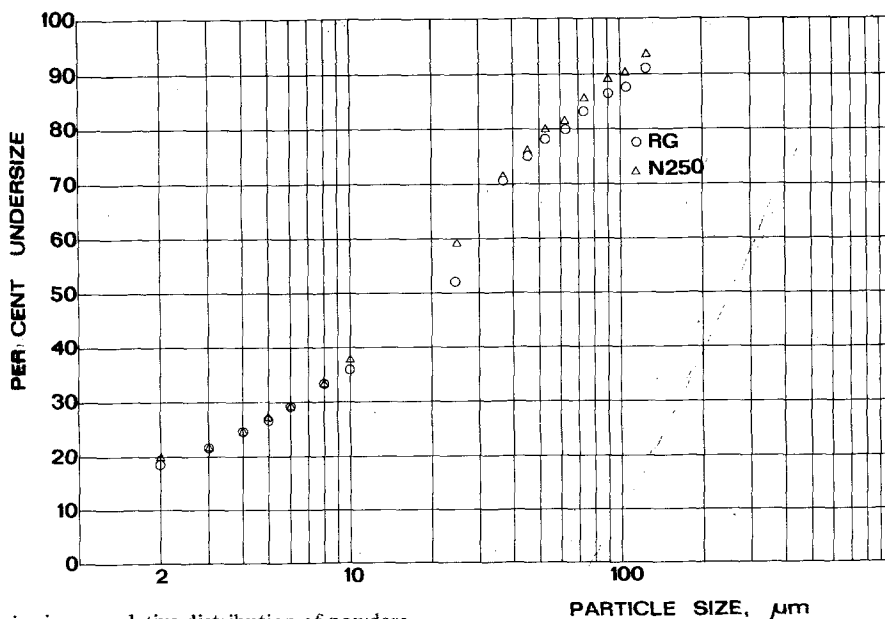


Figure 1 Grain size cumulative distribution of powders.

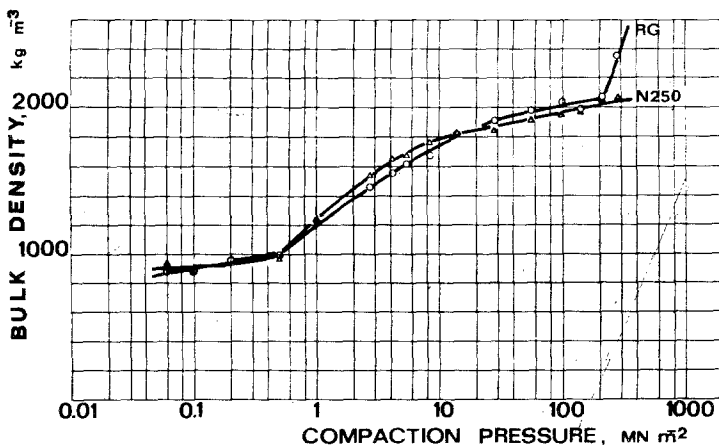


Figure 2 Pressure-compaction data of the powders.

related to the well-known semilogarithmic relation between the mechanical strength of brittle materials and their bulk density, at least in the high pressure range [10–13]. The changes in the slope of such curves can sometimes be related to different mechanisms of powder compaction. In the present case, the complexity of the behaviour must be related to the composite nature of the powders, whose compaction behaviour needs further investigation. It was not, however, the purpose of this paper, and the compaction data of

the powders serve merely to evaluate their possible effect on the firing shrinkage. SEM examinations of the powders as well as of the compacts did not show any feature that would account for the observed compaction behaviour.

2.2. Firing

The compacts to be fired were formed in the rectangular die, by the same procedure quoted above, over the pressure range 14 to 280 MN m⁻². After drying at 100°C to constant weight, the

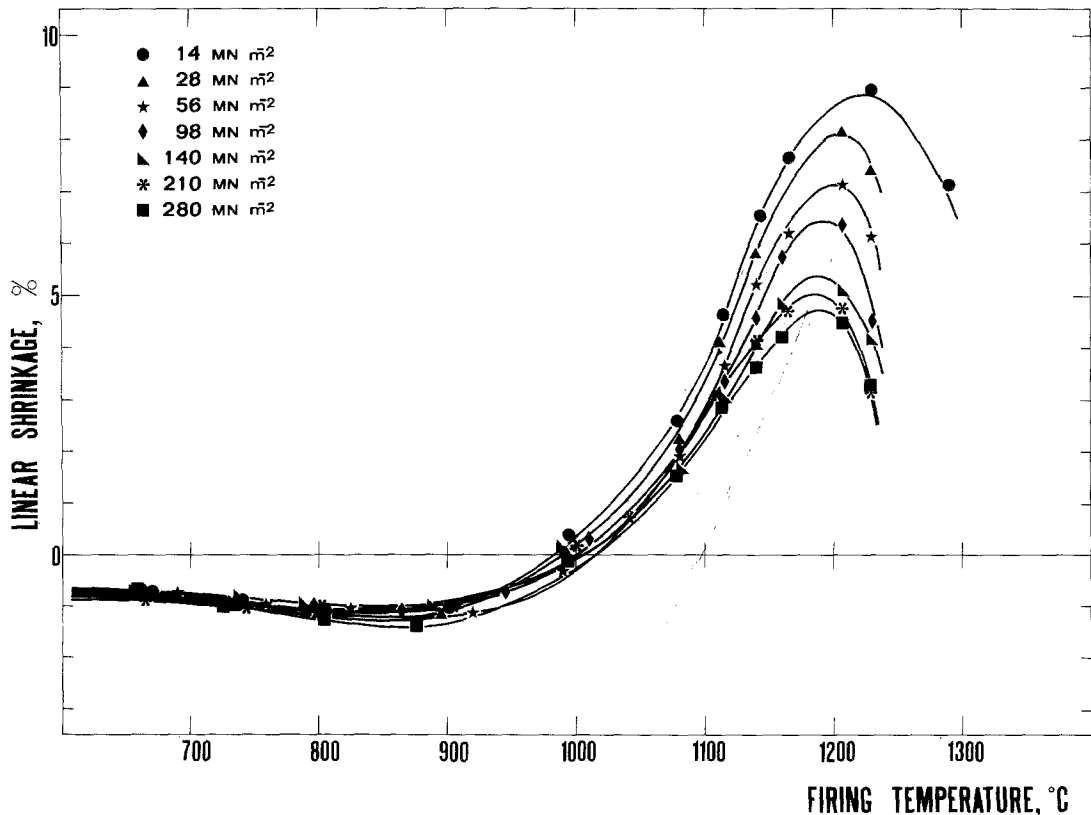


Figure 3 Linear per cent shrinkage of RG samples versus firing temperature.

samples were stored in a glass desiccator for future use. The samples were then fired in an electric kiln in air at temperatures over the range 700 to 1300°C. The firing schedule consisted of raising the temperature at 70°C h⁻¹ to the soaking temperature, soaking for 6 h and cooling at the same rate. This longer firing schedule compared to that used previously for the same materials [7] was required because the powders employed were not as fine. The linear per cent shrinkage and water absorption of the fired compacts were then determined according to UNI 6506-69 procedures.

3. Results and discussion

The linear per cent shrinkage and water absorption of RG compacts are plotted as a function of firing temperatures in Figs. 3 and 4. The behaviour for constant compacting pressures is closely similar to that reported elsewhere [7]. The negligible differences are probably related to both different grain size distributions of the powders and firing schedules. The linear per cent shrinkage and water absorption decrease with increasing compaction pressure for constant soaking temperatures, as well

as the maximum densification temperature, which may be referred to as the conventional firing temperature. Compacts of the two types of powders exhibit similar behaviour, except that narrower vitrification ranges and lower vitrification temperatures are obtained with those made from N 250 powder. This is to be expected, because the iron oxide content of the natural *Eurite* acts as a fluxing agent. For the same reason, the bloating processes occurring at higher temperatures [6, 7] are enhanced by the increase of the compaction pressure.

The linear shrinkage data are found to be linearly related to the logarithm of compaction pressure for constant soaking temperatures at or below those required for maximum densification, while at higher temperatures this linear relationship is not obeyed. In order to evaluate the adequacy of the correlation, a regression analysis of the data in the linear region was made. The results are given in Table II and plotted in Figs. 5 and 6 together with the experimental data. The analysis shows that the correlation coefficient increases with temperature to values very close to unity at the temperature of

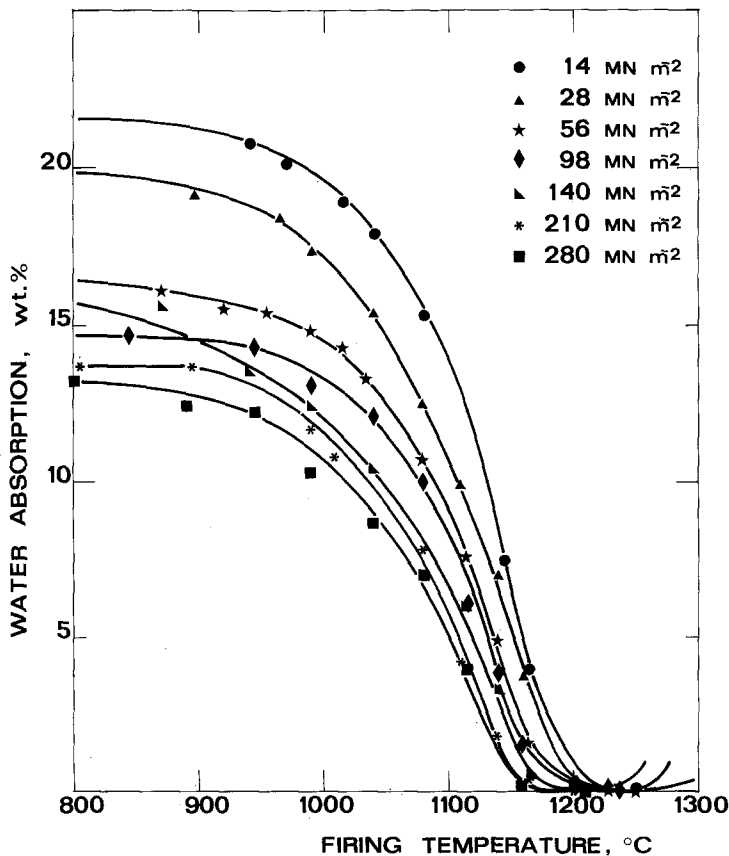


Figure 4 Water absorption of RG samples versus firing temperature.

TABLE II Regression line and correlation coefficient, r , at constant temperature (s : linear per cent shrinkage; p : compaction pressure)

T ($^{\circ}\text{C}$)	RG	r	T ($^{\circ}\text{C}$)	N 250	r
870	$s = -1.2 + 0.023 \ln p$	0.47	880	$s = -1.2 + 0.056 \ln p$	0.69
1040	$s = 0.97 - 0.055 \ln p$	0.62	1040	$s = 1.4 - 0.13 \ln p$	0.76
1080	$s = 3.2 - 0.27 \ln p$	0.92	1090	$s = 4.2 - 0.40 \ln p$	0.89
1140	$s = 8.7 - 0.89 \ln p$	0.99	1150	$s = 9.3 - 1.0 \ln p$	0.98
1230	$s = 14 - 2.0 \ln p$	0.99	1190	$s = 15 - 2.2 \ln p$	0.99

maximum densification. Correspondingly, X-ray diffraction analyses showed increasing vitrification of the samples. This linear behaviour is clearly not dependent on the compaction behaviour of the powders, if a comparison with the compaction data of Fig. 2 is made. The correlation coefficient decreases at higher temperatures, where other processes such as bloating occur and the linear relationship no longer is obeyed.

As quite different self-vitrifying materials as to powder characteristics and composition exhibit the same linear behaviour [1, 2], it can be inferred that this behaviour is chiefly related to the development of the glassy phases during firing. Moreover, for the same reason, this linear relationship does not seem to depend on the firing time and grain size distribution and not even on the die shape, as it was obtained also for cylindrical compacts [1, 2]. This behaviour is the opposite of that shown during initial sintering of some oxide powders with increasing green compact density, where, on the contrary, an increase of linear shrinkage was observed [14–17]. Shrinkage decreases with increasing compaction pressures were observed both in the solid state and liquid

phase sintering of metals systems and the like [18–21], but the relative interpretations do not seem to fit the present cases.

Although further investigations are needed, because of the complexity of these multiphase systems, some considerations can be made on the basis of the liquid phase sintering mechanisms commonly accepted [18, 22, 23]. Sintering in the presence of a liquid phase is the most common mode of densification in structural clay materials, technical porcelains and whitewares, where a liquid silicate is formed at the firing temperature and acts as a bond for the structure [25–31]. An increase of the compaction pressure certainly results in a better contact between particles and grains, and hence all the reactions, vitrification included, are accelerated [18, 32], thus resulting in a decrease of the firing temperature with increasing compaction pressures. On the other hand, the decrease of the linear shrinkage with increasing compaction pressure should surely be related to sintering phenomena in the presence of a liquid phase, such as particle rearrangement due to capillary forces of the forming liquid phase, filling of the pores and interstices between particles and grains by liquid

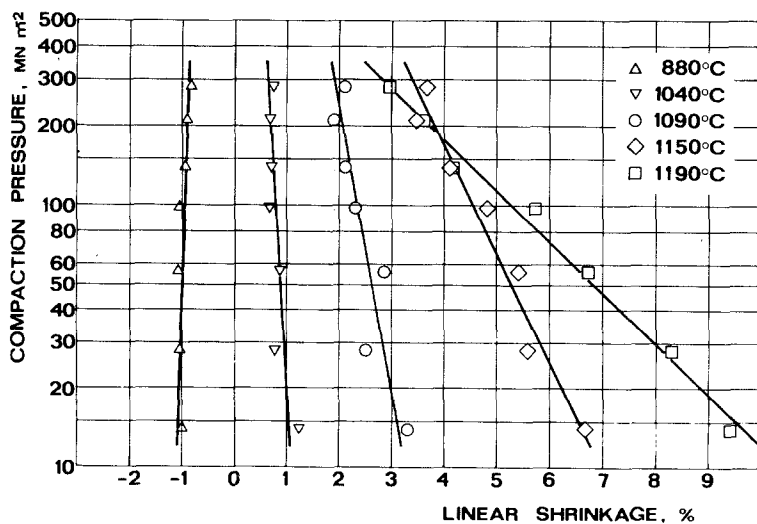


Figure 5 Linear per cent shrinkage of RG samples versus compaction pressure.

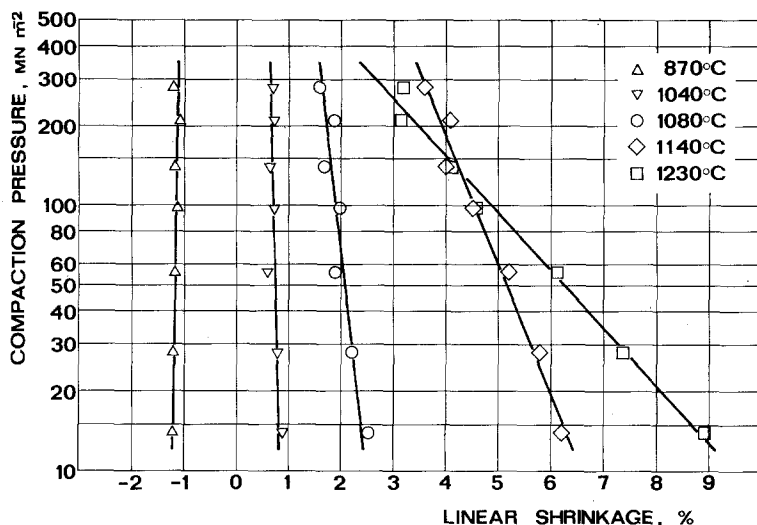


Figure 6 Linear per cent shrinkage of N 250 samples versus compaction pressure.

phase, etc. If some interlocking between grains of different hardness in these composite powders occurs at increasing compaction pressures, similar to particle wedging in metal powder systems during cold compaction [18, 33–35], a decrease of the linear per cent shrinkage should be expected. Other phenomena could also play a role, such as bloating of the glassy phase, wetting of solid particles by liquid phase, mutual solution and reaction of components, but nothing else may be said at this time. Further investigations are in progress on the sintering behaviour of these self-vitrifying materials, in order to achieve some interpretation of the linear relationship experimentally observed.

4. Conclusions

The following conclusions may be drawn from the experimental results and their discussion:

(1) The self-vitrifying ceramic materials investigated exhibit a firing shrinkage which decreases linearly with the logarithm of the compaction pressure within the vitrification temperature range.

(2) This behaviour appears to be chiefly related to the glassy phase development during firing, as it occurs for quite different self-vitrifying materials. When other phenomena occur in the glassy phase, such as bloating, this relationship is not obeyed any more.

(3) The compaction behaviour of the ceramic powders does not seem to influence the linear relationship between shrinkage and logarithm of compaction pressure.

(4) The presence of fluxing agents does not seem to affect this linear relationship, their effect

only resulting in changes of the vitrification temperature and ranges.

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