Study of the sintering mechanism of kaolinite at 900 and 1050°C; influence of mineralizers

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This paper presents a study, by means of isothermal dilatometry, of the often very important (10%) shrinkage phenomenon which occurs when heating clay ceramic materials, and especially of the influence of mineralizers on the shrinkage of kaolinite at 900 and 1050° C. We found that the isothermal shrinkage versus time curve of kaolinite at both temperatures was well described by the following equation:

$$\lambda = \frac{t}{\alpha + \beta t} \tag{1}$$

where λ is the linear shrinkage (relative to the initial length of the bar), t the time, and α and β two constants. The presence of various mineralizers at different concentrations did not affect the basic shape of this curve at either 900 or 1050° C, but affected the values of parameters α and β. A sintering mechanism is proposed which takes into account the most recent data concerning the structural transformation of kaolinite in the 900 to 1050° C temperature range. The kaolinite sintering mechanism is of the viscous-flow type proposed by Frenkel [1] involving an amorphous phase, the viscosity of which increases with time due to its progressive recrystallization. The influence of mineralizers is then explained in terms of their action on the viscosity of the amorphous phase and their action on recrystallization.

1. Introduction

Skrinkage during the heating of clay ceramic bodies is sometimes very important (10% and more), while at the same time, their mechanical strength may increase considerably. These two phenonema are related to sintering which affects clays as well as other powdered materials. Previous authors [2–4] have proposed interpretations of the shrinkage phenomena of kaolinite in terms of physical sintering. Discussions on sintering phenomena are usually based on simple geometric model, e.g. sphere-to-sphere.

The general relationship between the relative shrinkage λ, and the radius x of the contact circle between two spheres of the same radius r, is approximated by

$$\lambda = \frac{x^2}{2r^2}. \tag{1}$$

The smaller x is with respect to r, the better this approximation will be. Moreover, the most general equation describing sintering versus time is the following;

$$x^n r^{-m} = ct \tag{2}$$

where n and m are two constants related to the sintering mechanism, and c is a constant related to the various physico-chemical properties of the powder (surface energy, molecular weight, diffusion coefficients, viscosity, etc.) [5].

Combining Equations 1 and 2, one obtains the following general equation;

$$\lambda = ct^{2/n} r^{2(m/n-1)} \tag{3}$$

Table I lists some typical sintering mechanisms and the corresponding values of m and n.

Clearly, the above mechanisms only take into account materials in which no physico-chemical changes occur during sintering; this is not the case for clays and especially not for kaolinite [9–10].

TABLE I Some values n and m in the general equation of sintering, and the related expression of $\lambda x^n r^{-m} = ct$

Mechanism of sintering	Reference	n	m	Expression of shrinkage (λ)
Bulk diffusion	Kingery and Berg [6]	5	2	$ct^{2/5}r^{-6/5}$
Grain boundary diffusion	Kuczynski [7]	6	4	$ct^{1/3}r^{-2/3}$
Viscous flow	Frenkel [1]	2	1	ctr^{-1}
In the presence of a liquid phase	Kingery [8]	6	2	$ct^{1/3}r^{-4/3}$

The aims of this paper are to find the most probable sintering mechanism and to understand the effect of impurities on the densification process of kaolinite in the 900 to 1050° C temperature range, by interpreting the isothermal shrinkage curves. Mineralizers were dispersed in kaolinite according to a new patented process [11] in order to enhance their action. The most recent data on the structural changes occurring in pure or mineralized kaolinite in the 900 to 1050° C temperature range [10] will guide us in choosing and eventually modifying one of the already proposed sintering models.

2. Experimental
2.1. Materials and sample preparation
The clay used was the Kolloid kaolin from Karlowy Vary (Czechoslovakia); its characteristics are presented in Table II.

Various metal oxides were introduced in kaolin; these oxides were obtained in situ by thermal decomposition during heating of the corresponding nitrates previously dispersed in the crude material. The nitrates used were of analytical grade. The Mixing of each nitrate with the kaolin was effected by means of an agate-ball mill rotating at 800 rpm for 20 min. The concentration of the mineralizer M was expressed in molar percentage of the metal

TABLE II Characteristics of the Kolloïd kaolin

Chemical analysis		Rational analysis	(wt %)
Compound	(wt %)		
SiO_2	46.35	Clay subst.	98.9
Al_2O_3	38.72	Quartz	1.1
Fe_2O_3	0.87	Feldspar	0.0
TiO_2	0.15	Grain size	(wt %)
CaO	0.24		
MgO	0.02	$< 1 \mu m$	70
Alkalines	0.15	$< 2 \mu m$	90
		$< 3 \mu m$	93

salt, assuming the formula of kaolinite to be $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$ (Mol wt = 258). Each mix was maintained in dry powder form until extrusion in cylindric rods (diameter 5 mm). Before extrusion, distilled water was carefully added to the powder in order to obtain a plastic paste. Rods were dried, first in a drying stove (50° C, 90% r.h.), then in an oven at 200° C.

2.2. Dilatometric measurement apparatus
The apparatus used was the Chevenard–Joumier type constructed by ADAMEL (France), equipped with an open air sample holder. The rate of temperature rise was 5° C min^{-1}.

3. Results
3.1. General shape of the kaolin dilatometric curve
The general shape of the expansion/shrinkage versus temperature curve of kaolinite is well known to ceramicists and is shown in Fig. 1. This curve exhibits a maximum near 550 to 600° C, when kaolinite is transformed into metakaolinite by loss of its structural water. Near 900° C, there appears an initial shrinkage which proceeds to a limited value and levels off. Near 1000° C, a second shrinkage develops and continues at higher temperatures to the softening point of the ceramic. For convenience, the shrinkage starting at 900° C will be called "LT shrinkage" (low temperature shrinkage) and the one starting at 1000° C, "HT shrinkage" (high temperature shrinkage).
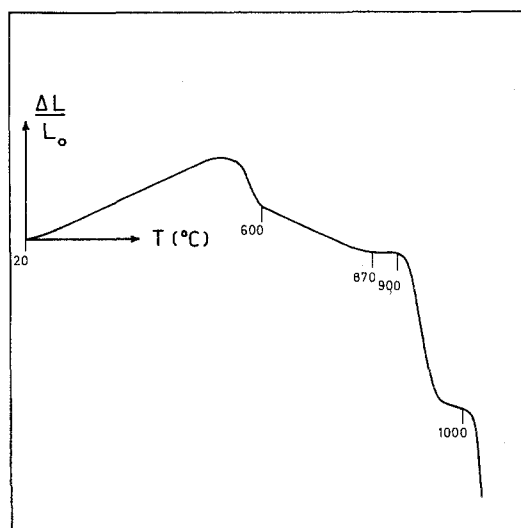

Figure 1 General shape of the expansion/shrinkage versus temperature diagram of kaolinite.
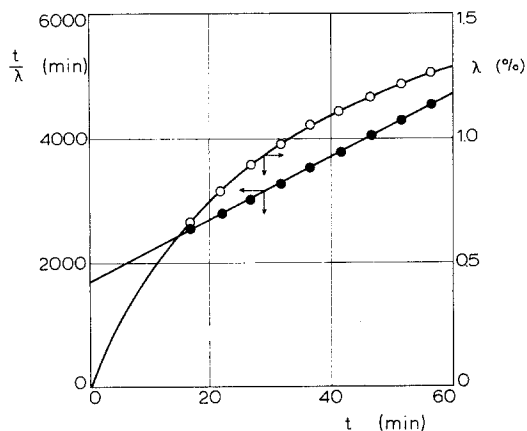
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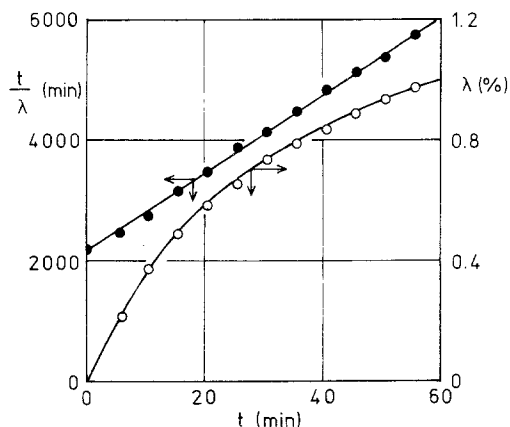*Figure 2* Shrinkage isotherm of Kolloïd kaolin at 900° C.

Figure 3 Shrinkage isotherm of Kolloïd kaolin at 1050° C.

3.2. General shape of the isothermal LT and HT shrinkage versus time curves

Figs. 2 and 3 (open circles) show respectively the experimental isothermic LT (900° C) and HT (1050° C) shrinkage curves of the pure kaolin, after a 5° C min^{-1} temperature rise.

3.3. Empirical equation of the isothermic shrinkage versus time curves of kaolin

The isorthermal shrinkage curves were found to obey the following equation;

$$\lambda = \frac{t}{\alpha + \beta t} \qquad (4)$$

where λ is the relative linear contraction of the rod, t the time and α and β two parameters. The significance of these two parameters is as follows;

$$\alpha^{-1} = \left(\frac{d\lambda}{dt}\right)_{t=0},$$

the initial shrinkage rate, and

$$\beta^{-1} = \lim_{t \to \infty} \lambda = \lambda_\infty$$

is the limit of shrinkage after an infinite time. α/β has the dimension of time: it is the time necessary to realize a shrinkage of $\lambda_\infty/2$ and called the "half shrinkage period". The reciprocal of the half shrinkage period could be called "relative shrinkage rate" as it is the initial shrinkage rate relative to the shrinkage limit.

Figs. 2 and 3 (black circles) show the very good fit between experimental points and the above equation; the experimental values of $t\lambda^{-1}$ are plotted versus t; the points fit straight lines, corresponding to the following equation, derived from Equation 2

$$t\lambda^{-1} = \alpha + \beta t. \qquad (5)$$

The slope of the straight line is β and its zero ordinate α. Since the isothermal condition is not instantaneously reached, a certain contraction has already occurred before the desired temperature is obtained. Consequently, the true origin of the isothermal shrinkage curve cannot be found experimentally. This difficulty is solved as follows.

On the shrinkage versus time curve (Fig. 4), a point O′ is chosen in the isothermal region II. Experimental points (τ, l) are taken on segment O′B. The equation of the shrinkage curve in the co-ordinate axes $(l, O′, \tau)$ is

$$l = \frac{\tau}{a + b\tau} \qquad (4a)$$

where τ is the time, l the linear contraction, a and b two constants, Equation can be written
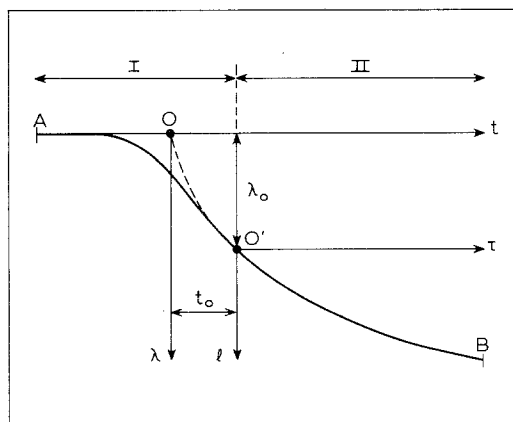

Figure 4 General shape of the shrinkage versus time curve of kaolinite: raising temperature region (I); isothermal region (II).

$$\tau/l = a + b\tau \qquad (5a)$$

By plotting the experimental values τ/l as a function of τ, we obtain a straight line; parameter a is the ordinate at the origin (O') and b is the slope. By extrapolation the true origin (O) of the isothermal curve can be computed and the equation in the co-ordinate axes (λ, O, t) can be formulated. The co-ordinates of the time origin (O) in the system (l, O', τ) are $(-t_0, -\lambda_0)$: λ_0 is measured on the experimental curve and is the linear shrinkage attained at O'. By simple substitution the relationship between a, b and α, β is obtained

$$t_0 = \frac{a\lambda_0}{1 + b\lambda_0} \qquad (6)$$

$$\alpha = \frac{a}{(1 + b\lambda_0)^2} \qquad (7)$$

$$\beta = \frac{b}{1 + b\lambda_0} \qquad (8)$$

3.4. Study on the LT isothermal shrinkage at 900° C

3.4.1. Influence of mineralizers

Experimental plots of $t\lambda^{-1}$ versus t for various mineralized samples (mineralizer concentration = 10 mol % are shown in Fig. 5. In all cases the shape of the LT isothermal shrinkage versus time curve is unchanged and obeys Equation 4. Values of α^{-1} and β^{-1} corresponding to each mineralizer are summarized in Table III, as they were determined by the method described in 3.3. The comparison of the respective influence of mineralizers on shrinkage parameters is illustrated in Fig. 6.
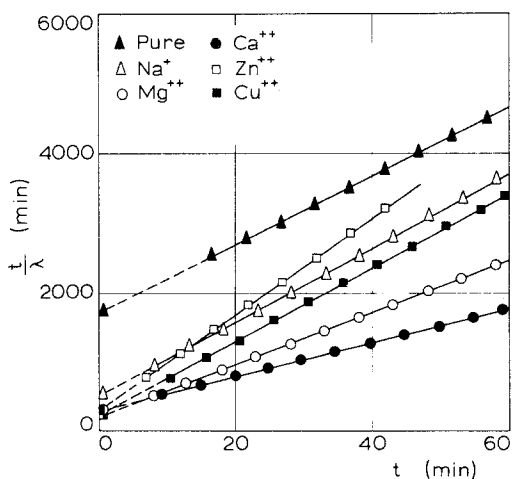

Figure 5 Experimental values of $t\lambda^{-1}$ versus t: influence of mineralizers (10 mol %) at 900° C.
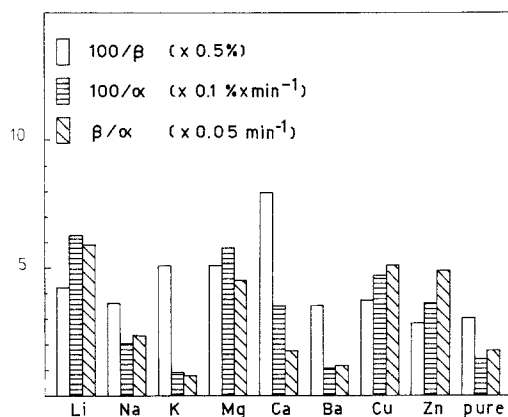

Figure 6 Influence of mineralizers (10 mol %) on the parameters of the LT shrinkage (900° C).

TABLE III Influences of mineralizers on the LT shrinkage ($T = 900°$ C).

Mineralizer (10 mol %)	$100/\alpha$ (% min^{-1})	$100/\beta$ (%)	β/α (min^{-1})
Li	0.64	2.16	0.30
Na	0.21	1.85	0.12
K	0.091	2.60	0.035
Mg	0.59	2.60	0.23
Ca	0.36	4.04	0.089
Ba	0.11	1.79	0.061
Cu	0.48	1.88	0.26
Zn	0.37	1.44	0.25
none	0.144	1.56	0.092

TABLE IV Influence of mineralizers concentration on the LT shrinkage; experiments with Mg and Ca ($T = 900°$ C).

Mineralizer	Conc. (mol %)	$100/\alpha$ (% min^{-1})	$100/\beta$ (%)	β/α (min^{-1})
none	—	0.144	1.56	0.092
Mg	2	0.10	2.08	0.048
	5	0.21	1.89	0.11
	10	0.59	2.60	0.23
	20	6.25	5.00	1.25
Ca	2	0.07	2.0	0.035
	5	0.09	2.29	0.039
	10	0.36	4.04	0.089
	20	2.90	10.4	0.28

3.4.2. Influence of mineralizer concentration: experiments with MgO and CaO

Results are summarized in Table IV and illustrated in Fig. 7; limit shrinkage λ_∞, (β^{-1}), is plotted versus mineralizer concentration in Fig. 7a, and initial shrinkage rate α^{-1} versus concentration in Fig. 7b. At equal concentrations shrinkage is more
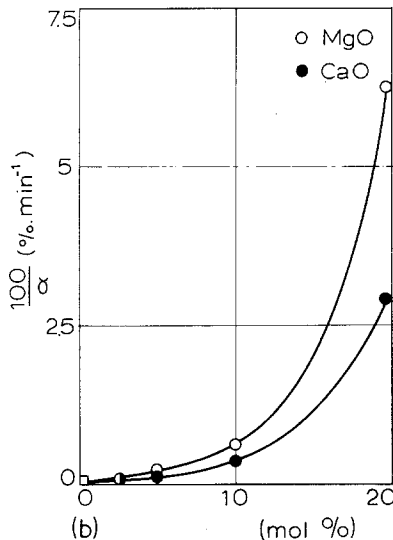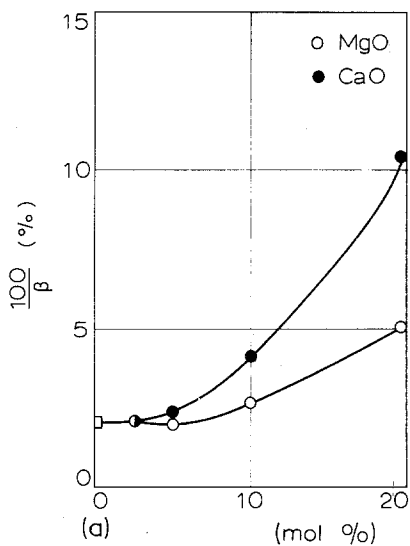
Figure 7 Influence of mineralizer concentration on the parameters of the LT shrinkage (900° C); experiments with Mg and Ca. (a) $100/\beta$ versus concentration; (b) $100/\beta$ versus concentration.
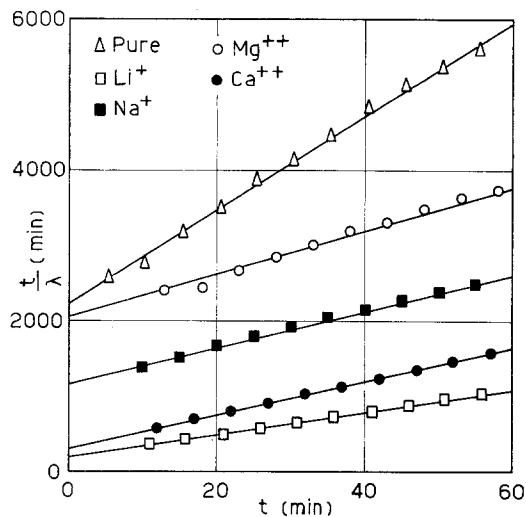

Figure 8 Experimental values of $t\lambda^{-1}$ versus t; influence of mineralizer (10 mol %) at 1050° C.

TABLE V Influence of mineralizers on the HT shrinkage ($T = 1050°$ C)

Mineralizer (10 mol%)	$100/\alpha$ (% min^{-1})	$100/\beta$ (%)	β/α (min^{-1})
Li	0.52	6.57	0.079
Na	0.087	4.12	0.021
K	0.086	4.49	0.019
Mg	0.049	3.52	0.014
Ca	0.32	4.57	0.070
none	0.046	1.58	0.029

TABLE VI Influence of mineralizer concentration on the HT shrinkage ($T = 1050°$ C); experiments with Mg and Ca.

Mineralizer	Conc. (mol%)	$100/\alpha$ (% min^{-1})	$100/\beta$ (%)	β/α (min^{-1})
none	–	0.046	1.58	0.029
Mg	2	0.057	2.2	0.026
	5	0.041	2.9	0.014
	10	0.049	3.5	0.014
	20	0.060	3.9	0.015
Ca	2	0.063	3.3	0.019
	5	0.062	4.3	0.014
	10	0.32	4.6	0.070
	20	0.047	0.8	0.059

important with CaO than with MgO, but the initial shrinkage rate is higher with MgO than with CaO.

3.5. Study on the HT isothermal shrinkage at 1050° C.
3.5.1. Influence of mineralizers
Experimental values of $t\lambda^{-1}$ versus time, corresponding to various mineralizers (concentration = 10 mol %) are plotted in Fig. 8. Values of α^{-1} and β^{-1} corresponding to each mineralizer are summarized in Table V.

3.5.2. Influence of mineralizer concentration: experiments with MgO and CaO
Results are summarized in Table VI and illustrated in Figs. 9a (limit shrinkage versus concentration) and 9b (initial shrinkage rate versus concentration). In the case where CaO is used as mineralizer, the
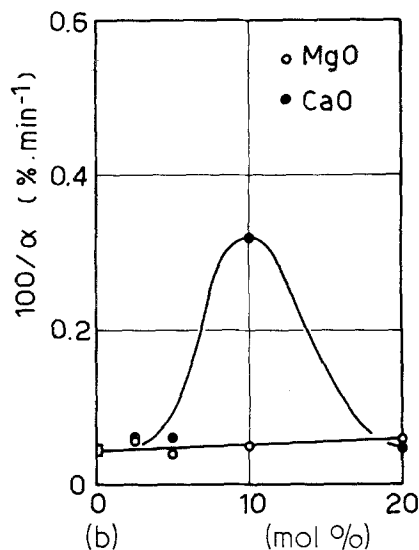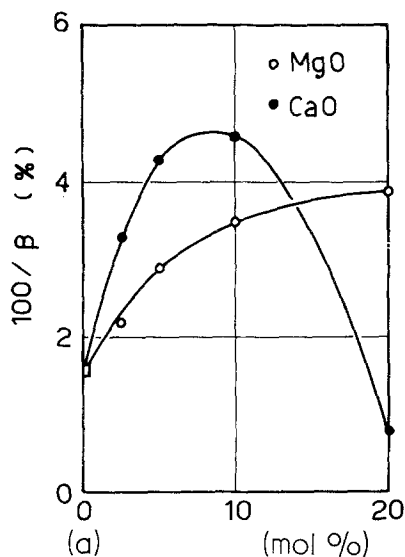
Figure 9 Influence of mineralizer concentration on the parameters of the HT shrinkage (1050° C); experiments with Mg and Ca. (a) 100/β versus concentration; (b) 100/β versus concentration.

shrinkage versus concentration curve is bell-shaped with the maximum occurring in the range 5 to 10 mol % (Fig. 9a); this is not the case for MgO. The same is observed for the initial shrinkage rate versus concentration curve (Fig. 9b).

4. Discussion
As it was shown in Section 3.3., the LT, as well as the HT, shrinkage curves of kaolinite, pure or containing various amounts of mineralizers, are very well described by an empirical law which we will call for convenience the "hyperbolic shrinkage

law". Linear correlation between t and experimental $t\lambda^{-1}$ values was better than 0.98.

This hyperbolic shrinkage law does not seem to be related to any of the classical sintering models presented in the introduction. Recent results concerning phase transformations in kaolinite in the 900 to 1050° C temperature range [10] have brought new information which we will try to use to interpret the hyperbolic law. These result show that the pseudo-lattice of metakaolinite breaks down at approximately 900° C into an amorphous structure. This breakdown occurs just at the start of the LT shrinkage, and therefore we may reasonably assume that the amorphous character of kaolin above 900° C results in an increased plasticity of the material, thus allowing sintering and shrinkage to occur.

The simplest sintering mechanism we may then look for, is a viscous-flow model very similar to the one proposed by Frenkel [1]. Its mathematical expression in terms of shrinkage is

$$\lambda = \frac{k\sigma t}{\eta r}, \qquad (9)$$

where λ is the relative linear shrinkage, t the time, r the grain size, η the apparent viscosity of the material (reciprocal of plasticity), σ the surface tension of the solid and k a proportionality constant. Furthermore, the results concerning the structural evolution of kaolinite show that the amorphous phase produced by the breakdown of metakaolinite at 900° C progressively crystallizes into quartz, γ-alumina and mullite. The sintering ability of the material must therefore decrease progressively as its amorphous character diminishes, i.e. as if the apparent viscosity of the solid was increasing with time.

It seems reasonable to suppose that, in the first stage of kaolinite sintering, the only parameter affected by its structural evolution will be η; this is equivalent to saying that the driving force of sintering (surface tension σ) remains constant. As a first approximation, we will assume that the apparent viscosity of the solid increases linearly with time. Such a hypothesis is expressed as follows:

$$\eta = \eta_0 (1 + \epsilon t), \qquad (10)$$

where η_0 is the initial apparent viscosity, and ϵ the rate of increase of viscosity. Introducing Equation 9 we obtain

$$\lambda = t \Big/ \left(\frac{\eta_0 r}{\sigma k} + \frac{\eta_0 r \epsilon}{\sigma k} t \right) \qquad (11)$$

This expression is clearly identical to the emprical hyperbolic law, in which α and β are defined

$$\alpha = \frac{\eta_0 r}{\sigma k} \qquad (12)$$

$$\beta = \frac{\eta_0 r}{\sigma k} \epsilon \qquad (13)$$

From Equations 12 and 13 we see that β^{-1} and α^{-1}, respectively the limit shrinkage and the initial shrinkage rate, are proportional to the reciprocal of the initial viscosity η_0. Furthermore, β is proportional to ϵ, the rate of increase of viscosity. The latter is, in fact, identical to ratio β/α which had already been defined as the relative shrinkage rate (see Section 3.3).

4.1. Influence of mineralizers on the LT Isothermal shrinkage

From the Equation 12, the initial shrinkage rate may be taken as a measure of the action of mineralizers on the initial viscosity of kaolin during sintering, provided others parameters remain approximately constant. Besides, the relative shrinkage rate ϵ is a measure of the amorphous phase recrystallization rate.

Initial shrinkage rates of $900°$ C of various mineralized kaolin samples are plotted versus the corresponding mineralizer ionic radii in Fig. 10a (concentration = mol%). The points fit fairly well on a curve left to right decreasing. This is consistent with the intuitive picture which suggests that the smaller the ionic radius of a given mineralizer, the easier its diffusion will be through the metakaolinite lattice and the more quick and complete will be the breakdown of the latter into an amorphous phase. The result of this will be an increased plasticity and higher initial shrinkage rate.

Experimental values of β are plotted in Fig. 10b versus the corresponding values of α from the same samples as above. Clearly, the slope of the straight line joining each of these points to the origin is β/α, i.e. ϵ, the rate of increase of viscosity of the corresponding sample. Fig. 10b shows that experimental points are divided into three groups. Two of these are fitted by straight lines passing through the origin, and thus correspond to samples with approximately the same ϵ value.
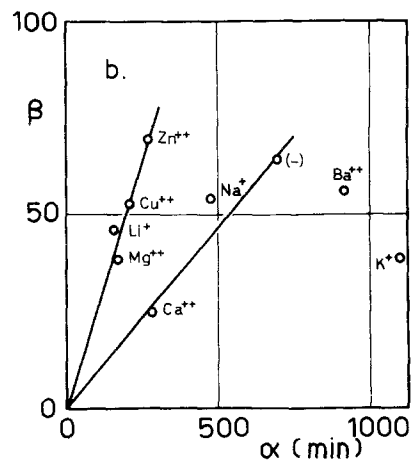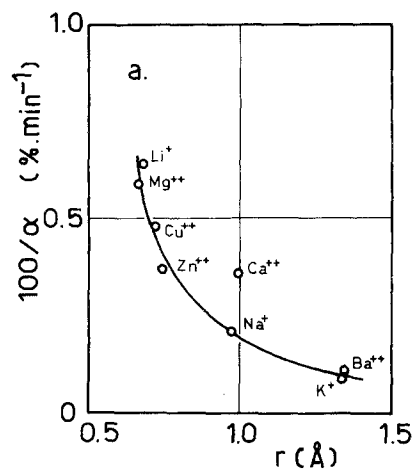
Samples mineralized by Li, Mg, Cu and Zn

Figure 10 (a) Correlation between the initial rate of the LT shrinkage ($900°$ C) and the ionic radii of the mineralizers (10 mol%). (b) Values of β versus α of mineralized kaolinite samples (10 mol%); $900°$ C.

belong to the first group (Group A) and bear the highest ϵ. Such mineralizers are thus the most efficient for increasing the recrystallization rate of metakaolinite.

Samples mineralized by Na and Ca belong to the same group as pure kaolin (Group B); such mineralizers do not have marked influence on the recrystallization rate of metakaolinite.

Samples mineralized by K and Ba belong to a third group (Group C). Their representative points are not aligned with the origin; the corresponding ϵ values are very low as compared to the pure kaolin sample. Such mineralizers thus slacken the recrystallization of metakaolinite.

The above conclusions agree with previous results [9] concerning the influence of mineralizers

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TABLE VII Influence of mineralizers on the temperature of the exothermic peak of kaolinite

Mineralizer (10 mol %)		Peak temperature (°C)
A	Li	951
	Mg	960
	Cu	952
	Zn	938
B	Na	958
	none	970
	Ca	979
C	K	977
	Ba	984

on the 950° C exothermic reaction of kaolinite: all mineralizers from Group A bring down the exothermic peak temperature; on the other hand, mineralizers from group C raise this temperature (Table VII).

4.2. Influence of mineralizers on the HT shrinkage

HT isothermic shrinkage curves are described by the same hyperbolic law as the LT ones, indicating that the two sintering mechanisms are probably of the same nature. The increased plasticity of kaolin at 1050° C should then find its origin in a decreased stability of transitory phases (quartz, amorphous silica and γ-alumina) identified at 900° C. These transformations could somehow induce increased plasticity of the whole material. The fact that an important amount of free silica still remains amorphous in kaolin, even when heating for tens of hours at 900° C, has been observed previously [10]. This amorphous silica is probably still present when the HT shrinkage starts. In addition, one cannot disregard the possible occurrence of a melted phase, chiefly when alkali—metal oxides are added to kaolin.

The cause of the HT shrinkage seems very complex in nature. This complexity could account for the non-correlation between HT shrinkage parameters versus mineralizer ionic-radius. Since the structural evolution of kaolinite before HT shrinkage depends on the nature of the mineralizer present, the parameters of the HT shrinkage would be influenced, not only by ionic mobility of the mineralizer, but also by the exact nature of the crystalline changes involved. Moreover, microstructure modifications following LT shrinkage, whose importance varies from one mineralizer to another, can also influence the HT shrinkage parameters.
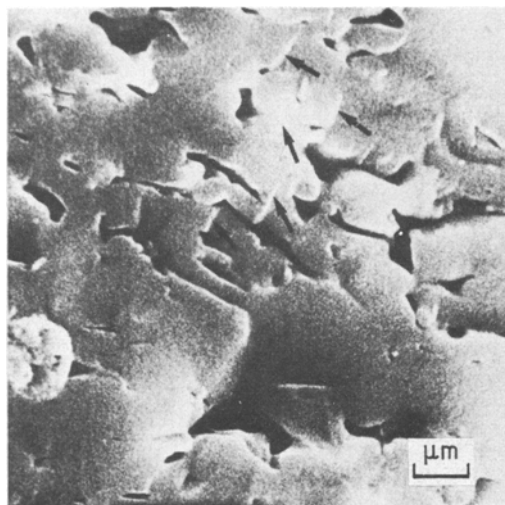

Figure 11 Microstructure of kaolinite mineralized with Ca (20 mol %), heated for 24 h at 900° C (10 000X).

Keeping this in mind, one can understand why the HT shrinkage versus CaO-concentration curve (Fig. 9a) is bell-shaped and why this is not the case with MgO. Fig. 11 is a scanning electron micrograph of a 20 mol % CaO mineralized kaolin sample, heated for 24 h at 900° C. Fig. 12 shows a kaolin sample prepared in the same conditions, but with MgO as a mineralizer. We see that porosity is still very important in the second sample while it has almost completely disappeared in the first. The HT shrinkage is clearly limited in the first sample due to the very reduced porosity, rather than to other physico-chemical phenomena.
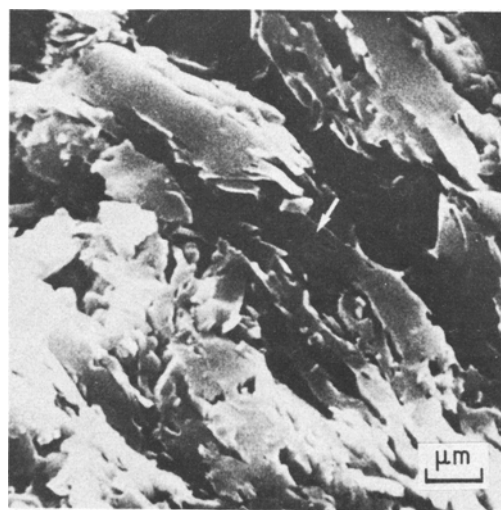

Figure 12 Microstructure of kaolinite mineralized with Mg (20 mol %), heated for 24 h at 900° C. (10 000X).

5. Conclusion

Isothermal shrinkage of pure or mineralized kaolinite, at both 900 and 1050° C, is very well described by the empirical "hyperbolic shrinkage law". From this law, a sintering mechanism for kaolinite has been inferred, consistent with the most recent results concerning the structural evolution of this material. The 900° C LT shrinkage mechanism could be of the viscous-flow type. Recrystallization of the amorphous phase produced by the break-down of metakaolinite could progressively slacken the flow. The influence of mineralizers would then be two-sided: they modify the initial viscosity of the body, and the amorphous phase recrystallization rate. The increased recrystallization rate thus results in a decreased shrinkage amplitude, while an increased initial shrinkage rate results from an increased ionic mobility of the mineralizer. The 1050° C HT shrinkage mechanism is probably more or less similar. Here, increased plasticity could find its origin in the instability of transitory phases and their transformation into high temperature ones. When alkali-metal oxides are used as mineralizers, the occurrence of a melted phase cannot be neglected.

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