

Chapter 2: Green processing

2.1 Introduction

This chapter primarily gives an overview of literature deemed relevant to the green processing of diamond-alumina.

Fabrication of ceramics from powders comprises two steps. The first step is green processing where the raw powder is formed into the so-called green body. A green body should roughly have the required shape of the desired final product and it has to stand up to some handling. In the second step, the green body is fired to bond the constituent particles and give the product its final strength.

Filter casting was chosen from several options as the green wet processing route to be used in this study, as discussed in the following section (section 2-2).

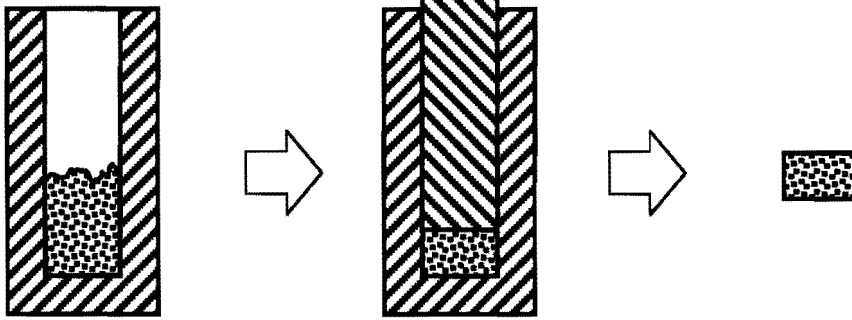
Literature references in this chapter were chosen for their relevance to the processing of suspensions of submicron suspensions. The experimental conditions of references are summarised in table 2-1 at the end of the chapter.

2.2 Motivation for filter casting

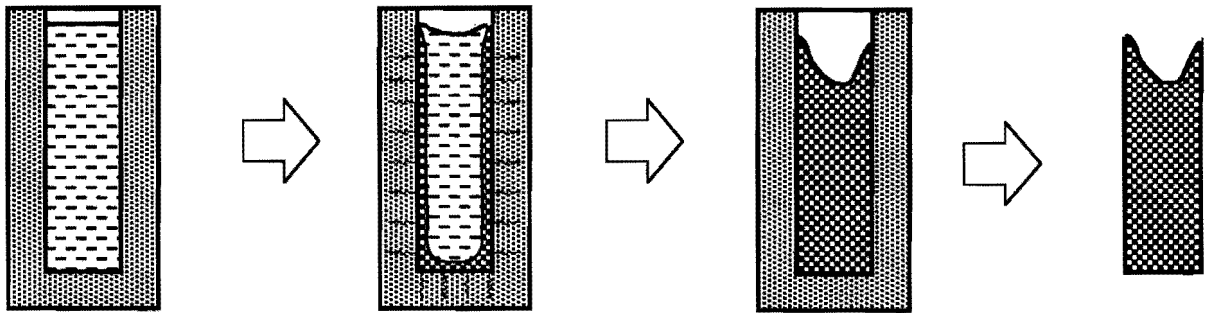
Green processing can be performed in various ways. For the purpose of discussion, the possible methods of green body formation are divided into 'dry' and 'wet' processing routes. In fig. 2-1 some green body formation methods are illustrated. Dry pressing is a common 'dry' processing route. In dry pressing, a dry powder is pressed into shape in a die. 'Wet' processing includes methods like slip casting, filter casting, and centrifugal casting. In slip casting, a suspension ('slip') of particles is poured into a porous mould. The suspending liquid is withdrawn into the mould by capillary force, eventually leaving the consolidated particles in the mould. After total consolidation the wet green body is removed from the mould and dried. The mechanism of filter casting is similar to slip casting. In filter casting the suspending liquid is filtered from the suspension by the application of pressure, followed by the drying of the wet green body. In centrifugal casting, the particles in a suspension are forced to settle from the suspension by centrifugation.



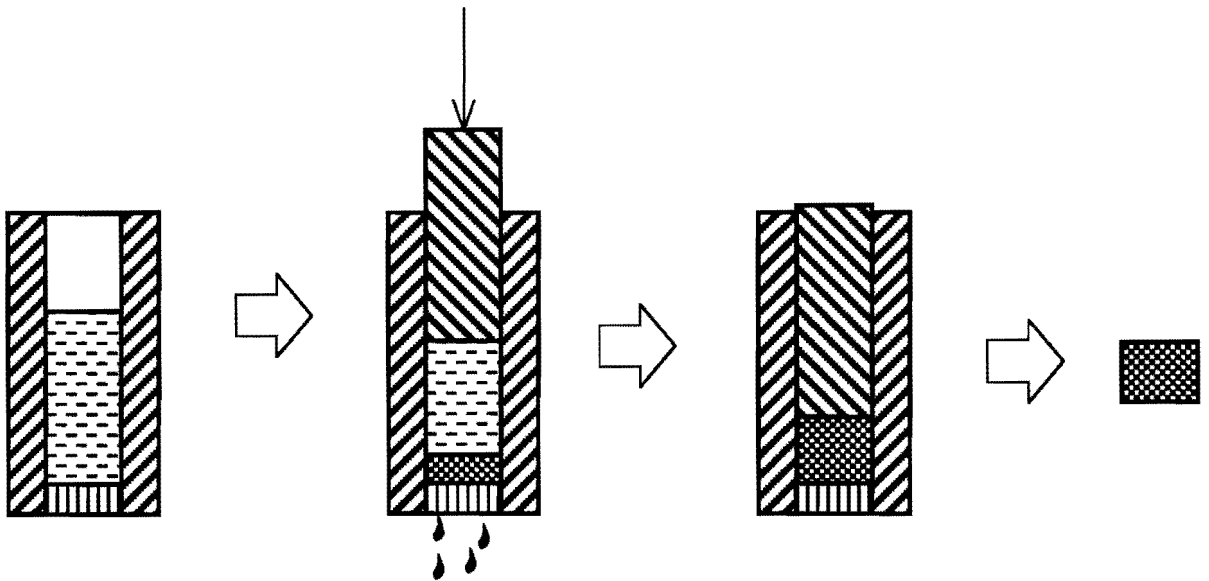
Dry pressing



Slip casting



Filter casting



Centrifugal casting

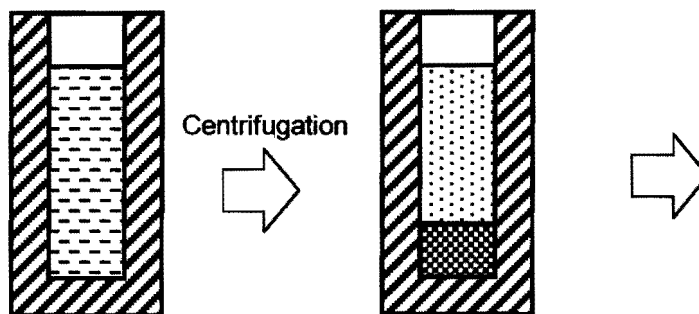


Fig. 2-1: Diagrammatic comparison of green body formation methods.

A green body should have a compact particle arrangement, but particles should be evenly distributed. Uneven distribution is usually due to so-called hard agglomerates that were originally present in the raw powder and were not broken during green processing. If the green body is not compact, a longer firing time or higher firing temperature might be required to fully densify the compact in the firing step. In the case of diamond-alumina composites, these more aggressive firing conditions might lead to damage to the diamond particles, as is discussed in chapter 3. If particles are unevenly distributed, the fired body might also have an uneven microstructure of inferior quality.

The compactness of particle arrangement is easily evaluated by measuring the green body's density. Even distribution is not defined and measured as easily. A possible way of quantifying the evenness of distribution is by mercury porosimetry, as was done by Roosen and Bowen (1988). The presence of areas where particles are more closely associated, which corresponds with an uneven microstructure, would show up as larger volumes of coarse pores. The principles of mercury porosimetry are discussed in section 2.3.1.

Roosen and Bowen showed that 'wet' processing is generally superior to dry processing, both in terms of achieving maximum green density and in terms of achieving a finer green structure, provided that particles are properly dispersed. A detailed discussion of the conditions necessary for proper dispersion is beyond the scope of this work, but alumina disperses well in suspensions of low pH of around 4. In fig. 2-2 it is shown that wet processed suspensions of low pH (less than 4.5, i.e. well dispersed) gave green bodies with relative densities of greater than 60 %, whereas no dry pressed green bodies did.

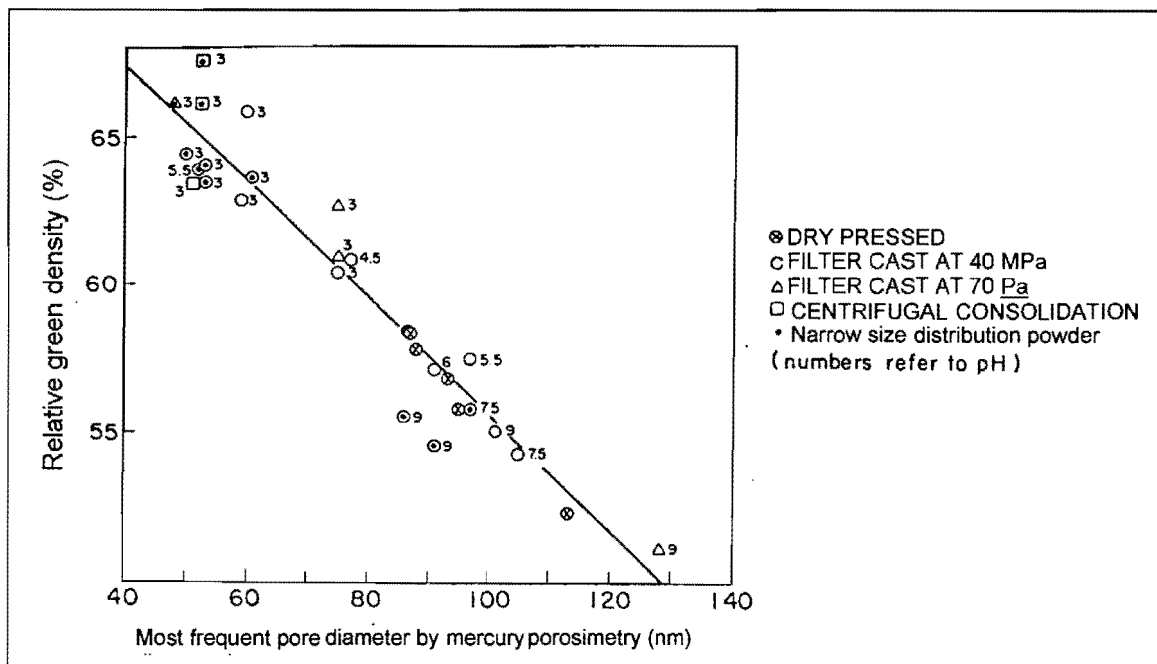


Fig. 2-2: Green density as a function of green microstructure. The data points were determined with different consolidation methods (both 'wet' and 'dry') and under varying conditions. Suspensions were prepared from two powders: A narrow and a wide particle size distribution. (From Roosen and Bowen, 1988). Suspensions with pH values ~4 can be considered to be well dispersed.

Having shown that 'wet' processing is preferable to dry processing, one is left with the choice of the specific 'wet' route, i.e. slip casting, filter casting or centrifugal casting. Since equipment for slip casting and filter casting are easy to manufacture and operate, centrifugal casting is not a good choice. This leaves slip casting and filter casting. The rate of consolidation in both slip casting and filter casting is determined by the size of the suspended particles (see section 2-4). Suspensions of finer particles take longer to consolidate, with the time required for the consolidation of the same volume of suspension being inversely proportional to the square of particle size:

$$t_{\text{fin}} \propto \frac{1}{d_{\text{part}}^2} \quad \ddagger \quad (2-1 / A1-40^{\S})$$

Slip casting is commonly used to process powder with coarse (roughly larger than 1 μm) particles. However, with the particles used in this study being an order of magnitude smaller than the usual micron-sized particles, time required for slip casting would have been in the order of 100 times longer than that required for micron-sized powders. This left filter casting as the chosen green processing route for this study.

2.3 The measurement of green properties

2.3.1 Density

The density of non-porous samples is easily measured by immersion in water (the 'Archimedes method'), with the density given by

$$[\text{Density}] = \frac{[\text{Weight in air}] \times [\text{Density of water}]}{[\text{Weight in air}] - [\text{Weight in water}]} \quad (2-2)$$

The density of porous samples (like green bodies) cannot be measured in this way, as intrusion in the pores would give a false value for the immersed weight. Instead, the fact that pores in a wet green body are completely filled with water was used to approximately determine green density. Density of a green body relates to its dry and wet weight as follows[#]:

$$[\text{Green density}] = \frac{[\text{Dry weight}]}{\frac{[\text{Wet weight}] - [\text{Dry weight}]}{[\text{Density of water}]} + \frac{[\text{Dry weight}]}{[\text{Particle density}]}} \quad (2-3)$$

Conceptually it is useful to express density relative to the true density, i.e.

[‡] Derived in appendix A1.

[§] The second number "A1-40" refers to the number used in appendix.

[#]
$$[\text{Green density}] = \frac{[\text{Dry weight}]}{[\text{Total volume}]} = \frac{[\text{Dry weight}]}{[\text{Volume of pores}] + [\text{Volume of solids}]} = \frac{[\text{Dry weight}]}{\frac{[\text{Wet weight}] - [\text{Dry weight}]}{[\text{Density of water}]} + \frac{[\text{Dry weight}]}{[\text{Particle density}]}}$$

$$[\text{Relative density}] = \frac{[\text{Measured density}]}{[\text{True density}]} \quad (2-4)$$

2.3.2 Mercury porosimetry (Smith, 1981)

Mercury does not wet most surfaces. This implies that pressure is needed to force mercury into pores. By immersing a sample in mercury and increasing pressure, mercury is forced into smaller and smaller pores. The pressure P required to force mercury into pores of size d_{pore} is

$$P = -\frac{4\sigma \cos \theta}{d_{\text{pore}}} \quad (2-5)$$

with θ the contact angle, as illustrated in fig. 2-3, and σ the surface tension of the mercury. In mercury porosimetry, 140° is normally used for θ on any surface. Surface tension of mercury is 0.47 N/m (Atkins, 1990). Substituting these values in equation 2-5 gives

$$d_{\text{pore}} = \frac{1440}{P} \quad (2-6)$$

with d in μm if P is in kPa . By measuring the volume of mercury penetrating at a given pressure, pore size distribution can be determined.

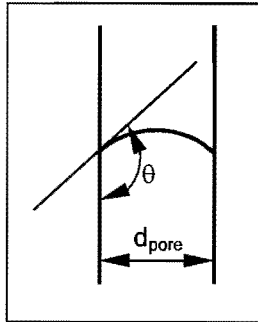


Fig. 2-3: Mercury penetration in a circular pore.

2.4 Consolidated layer growth

At the onset of filtration, particles in suspension are free to follow streamlines that form, and they move towards openings in the filtration medium. There some particles bridge and clog entrances to channels in the medium. This is a beneficial process since it blocks the migration of any further particles through the medium (Heertjes, 1964). Pores in the filtration medium therefore need not be smaller than suspended particles.

The initial clogging action is followed by the growth of the consolidated layer. The thickness of the consolidated layer L_{cl} at a time t is given by[‡]

$$L_{cl} = \sqrt{\frac{2k\Delta Pt}{z\mu_{sl}}} \quad (2-7 / A1-6)$$

where ΔP is the applied pressure difference across the filtration apparatus as illustrated in fig. 2-4. μ_{sl} is the viscosity of the suspending liquid. z is given by

$$z \equiv \frac{Q_{filt}}{Q_{cl}} = \frac{\epsilon_{susp} - \epsilon_{cl}}{1 - \epsilon_{susp}} \quad (2-8 / A1-20)$$

with Q_{filt} and Q_{cl} respectively the volume of filtrate and consolidated layer. ϵ_{susp} is the volume fraction of liquid in the unconsolidated suspension and ϵ_{cl} is porosity of the consolidated layer. k is the permeability of the consolidated layer. Permeability can be experimentally determined but it can also be predicted from other properties of the consolidated layer.

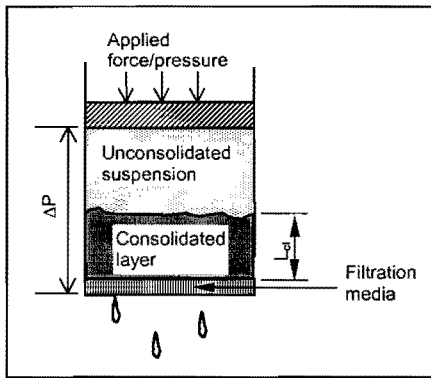


Fig. 2-4: Consolidated layer growth.

Equation 2-7 can be rewritten to predict the time needed to consolidate a given load of suspension. The alternative formulation was used in this study to determine the required 'dwell time' for filter casting. If a filtration device is initially loaded to a depth $L_{susp,0}$ then the time needed to fully consolidate a suspension is[‡]

$$t_{fin} = \frac{z\mu_{sl}L_{susp,0}^2}{2(1+z)^2 k\Delta P} \quad (2-9 / A1-10)$$

It is possible to determine t_{fin} because z is known from equation 2-8, μ_{sl} can be approximated as the viscosity of water (c. 1 mPa.s), k can be approximated as shown in the following paragraph, and ΔP is known from the filtration device set-up.

There are a variety of models which predict permeability but the Carmen-Kozeny equation is most commonly used. The Carmen-Kozeny model gives permeability as[‡]

[‡]Derived in appendix A1.

$$\lambda = \frac{\varepsilon_{cl}^3}{\theta \tau^2 (1 - \varepsilon_{cl})^2 \zeta^2} \quad (2-10 / A1-33)$$

with ε_{cl} the porosity of the consolidated layer, τ its tortuosity, ζ its specific surface area, and θ the Poiseuille factor. For the conditions of this work the following is true[‡]

$$\lambda \approx 1 \times 10^{-3} d_{part}^2 \quad (2-11 / A1-38)$$

Fig 2-5 gives the progress of consolidated layer growth, as predicted by equation 2-10 and 2-7, for a case typical of this study.

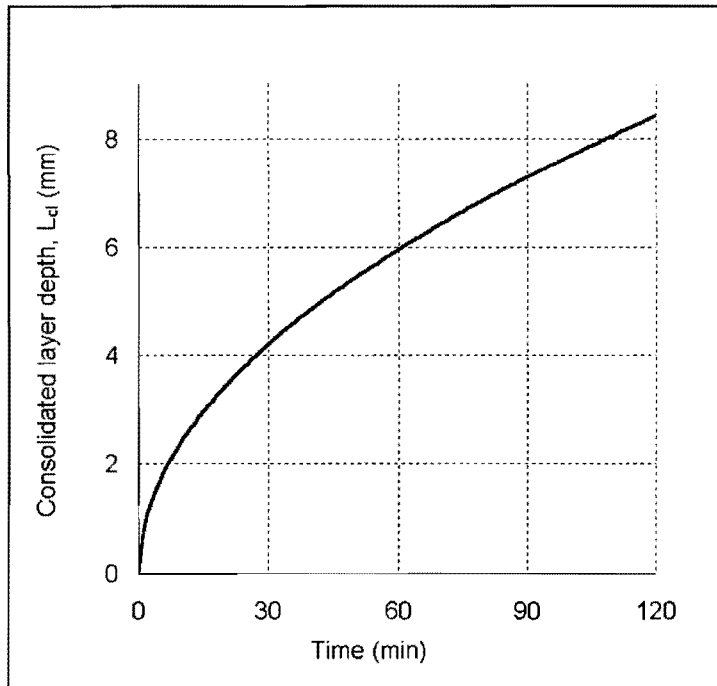


Fig. 2-5: Consolidated layer growth for the typical values of $\varepsilon_{cl} = 40 \%$, $\varepsilon_{susp} = 70 \%$, $\mu_{sl} = 1 \text{ cP}$, $d_{part} = 100 \text{ nm}$ and $\Delta P = 0.5 \text{ MPa}$.

2.5. Factors affecting green structure

2.5.1 Relationship between green texture and green density

In exhaustive work on green body formation, Roosen and Bowen (1988) investigated the effect various factors in cake formation. They quantified the texture of the green microstructure by mercury porosimetry (fine pores corresponding with a finer microstructure) and found the relationship already shown in fig. 2-2 where a finer structure is shown to correlate with a denser green body.

[‡] Derived in appendix A1.

2.5.2 Solids volume fraction in suspension

In filter casting, there are no clear trends on the effect of solids fraction in the suspension on the density of the green body formed from it. The results of Hampton *et al* (1988) and Velamakanni and Lange (1991) as given in fig. 2-6 and 2-7 are in conflict, giving both positive and negative trends. As Hampton *et al* (1988) and Velamakanni and Lange (1991) used different dispersion methods (deflocculent and pH, see table 2-1), these trends cannot really be compared. As seen in fig. 2-6 and 2-7, variations are smaller than 3 percentage points for both references. To a good approximation, one can therefore state that solids fraction does not have a significant effect on green density.

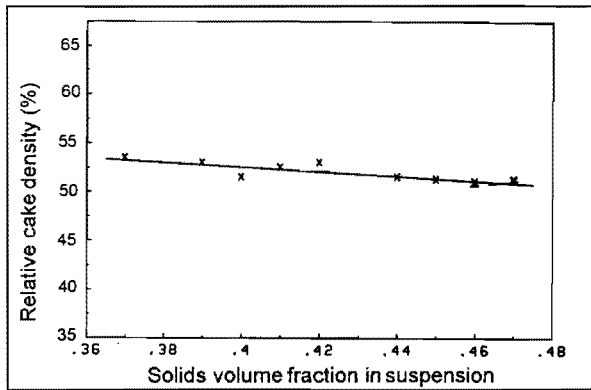


Fig. 2-6: The effect of solids volume fraction in suspension on green density as given by Hampton *et al* (1988).

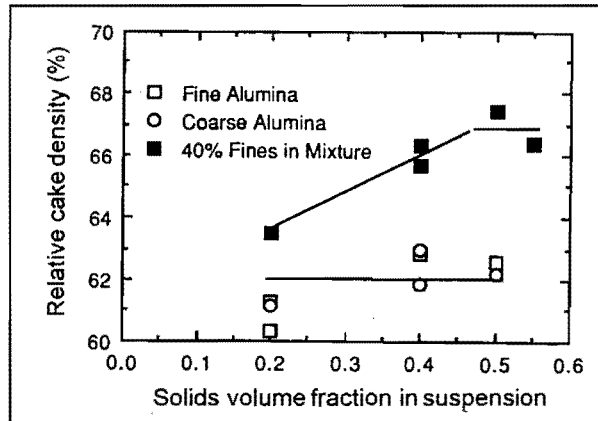


Fig. 2-7: The effect of solids volume fraction in suspension on green density as given by Velamakanni and Lange (1991).

2.5.3 Particle size distribution

A narrow distribution of particle sizes is desirable from a firing point of view, since it leads to fired microstructures having a narrow grain size distribution. Fired compacts with narrow grain size distributions generally have preferable qualities. However, higher green density occurs with wide distributions of particle sizes, as fine particles can fill the voids between coarser particles, as illustrated in fig. 2-8.

In work done specifically on filter casting Smith and Haerle (1995) and Smith and Haber (1995) used the particle distribution function

$$F(d_{part}) = \frac{d_{part}^{k_{SH}} - d_{smallest\ part}^{k_{SH}}}{d_{largest\ part}^{k_{SH}} - d_{smallest\ part}^{k_{SH}}} \quad (2-12)$$

where F is the cumulative fraction of particles smaller than a d_{part} . They showed experimentally that the closer the modulus k_{SH} is to 0.37 the greater the green density. This implies that particle size distribution can be adjusted to give a maximum green density (on the condition that suspensions are well dispersed).

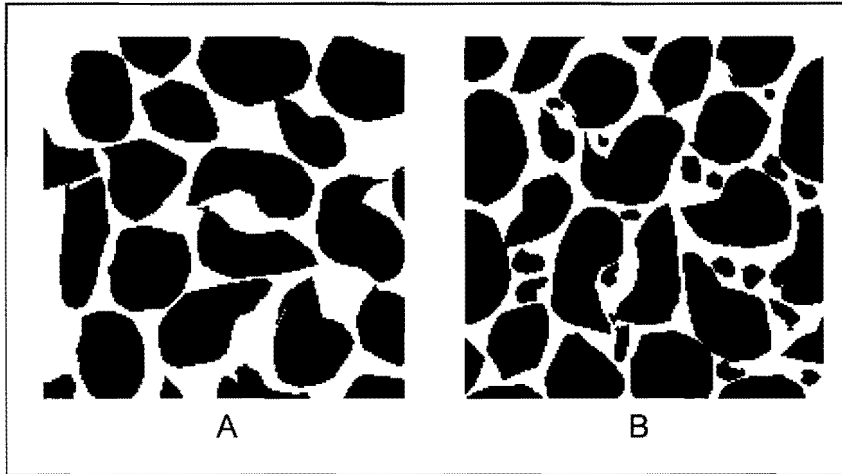


Fig. 2-8: Particle packing with narrow (A) versus wide (B) size distributions. The wide size distribution is seen to fill space more efficiently.

2.5.4 Pressure

Lange and Miller (1987) found no significant dependence on pressure for dispersed suspensions. With flocculated suspensions, however, they found that cake density increased considerably with increasing pressure as seen in fig. 2-9.

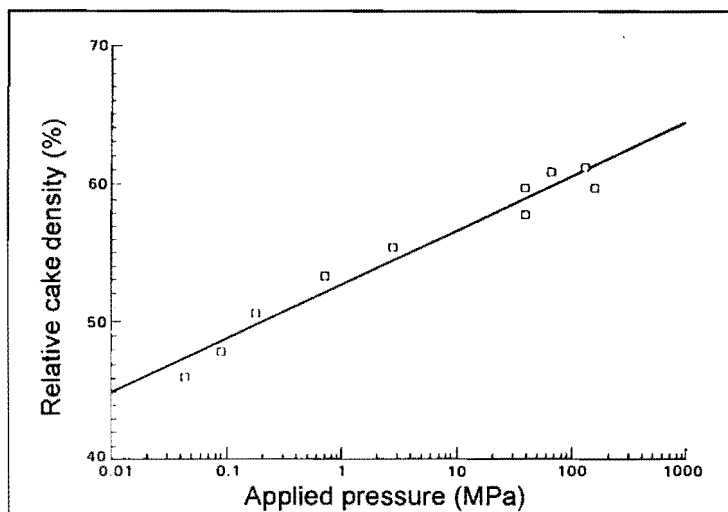


Fig. 2-9: The pressure dependence of solids loading on green density for flocculated suspensions subjected to filter casting at the indicated pressure (Lange and Miller, 1987).

Straight filtration of flocculated suspensions at low pressure does therefore not yield green densities comparable to those from the filtration of dispersed suspensions at equally low pressure. This is unfortunate, since green bodies formed from flocculated suspensions have the advantage of experiencing less separation with regard to particle size and components. In flocculated composite suspensions, particles of different components and sizes are fixed into flocs which do not break down during consolidation into the cake. The cake would therefore retain the state of mixture that existed in the unconsolidated flocculated suspension. In filtration of dispersed suspensions this advantage is lost, and particles of different components are free to separate under influence of other forces such as differences in their density.

Prevention of component separation by using flocculated suspensions was not employed in this study.

2.5.5 Suspension viscosity

A detailed discussion of this effect is beyond the scope of this survey.

Although suspension viscosity itself is a function of other factors it can give one an idea of the quality of dispersion. Low viscosity is generally characteristic of well-dispersed suspensions which leads to denser compacts (Smith *et al*, 1994; Chou and Senna, 1987).

2.6. Recovery strain

Lange and Miller (1987) also conducted research to determine the amount of deformation of green bodies after filtration, i.e. upon removal of pressure. In fig. 2-10 recovery strain between green bodies formed from flocculated and dispersed suspensions is compared. It can be seen that green bodies formed from flocculated suspensions show gradual 'recovery' of up to 2.8 %, while green bodies formed from dispersed suspensions 'recover' rapidly and 'recover' to the slightly smaller extent of 2.2 %. It cannot be imagined that all sections of a wet green compact would always recover at the same rate in all its sections. The recovery strain effect could therefore lead to cracking of the wet green compact.

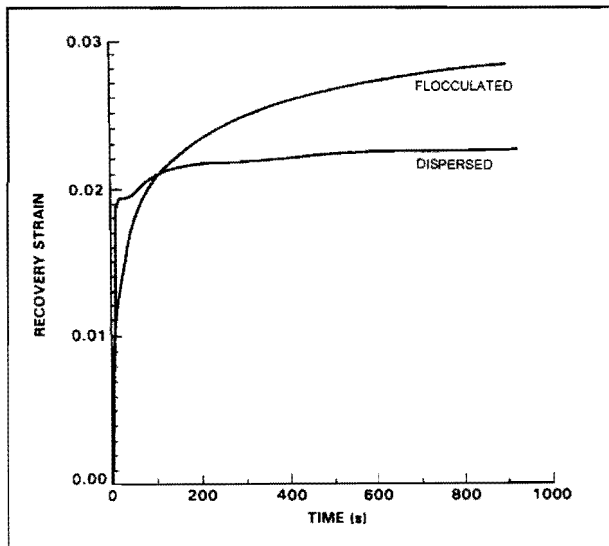


Fig. 2-10: Strain 'recovery' of green bodies formed from flocculated and dispersed suspensions after unloading from a filtering pressure of 80 MPa (Lange and Miller, 1987).

2.7 Non-homogeneity in green bodies

2.7.1 Separation of particle sizes

The consolidated layer growth kinetics in section 2.4 assumes a homogeneous consolidated layer by accepting a pressure gradient and constant porosity. In practice neither of these assumptions may hold.

Hampton *et al* (1988, 1992), for instance, conducted work on fine particle migration during filtration. They filtered suspensions of mixtures of fine and coarse particles and found that substantial migration of fine particles towards the filtrate withdrawal side of the cake occurred. Fig. 2-11 shows a substantial concentration of fine particles at the bottom of the cake after filtration.

2.7.2 Separation of composite suspension components

Lange and Miller (1987) and Aksay *et al* conducted filtration with suspensions made of alumina zirconia composite powders. No mention was made of segregation of alumina and zirconia. Chang *et al* (1991) specifically investigated the mass segregation of alumina-zirconia composites, unfortunately with centrifugal consolidation. They found that mass segregation does not occur with flocculated and coagulated suspensions but that it does occur with disperse suspensions with a distinct higher concentration of zirconia towards the bottom of the cake.

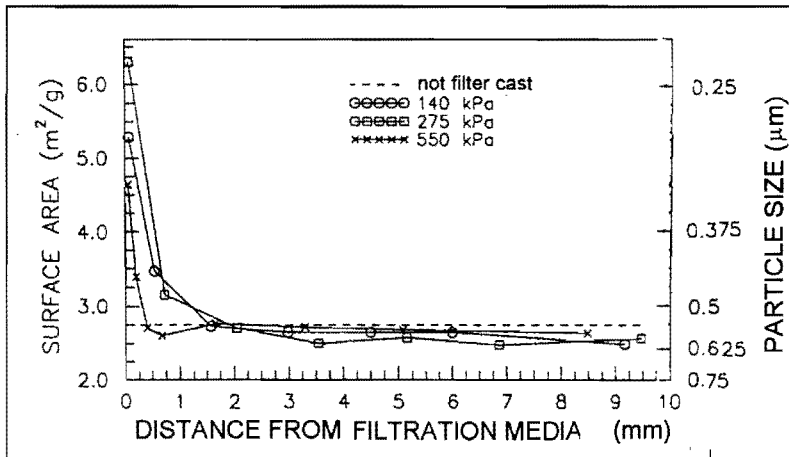


Fig. 2-11: Surface area and particle size versus distance above cake bottom for alumina. Pressures are the filter casting pressures. Surface area was determined by BET. The indicated particle size is the size based on the surface area ($d_{part} = 6/\sqrt{S}$). (Modified from Hampton et al, 1992).

Table 2-1: Some of the experimental conditions of authors referred to in chapter 2. The differentiation between 'fine', 'intermediate' and 'coarse' is arbitrary and does not have any special significance.

Authors		Hampton <i>et al</i> (1988)	Hampton <i>et al</i> (1992)	Velamakanni and Lange (1991)	Lange and Miller (1987)		Roosen and Bowen (1988)				Smith and Haerle (1995)	Smith and Haber (1995)
Description of work referred to		Effect of solids fraction in suspension	Fine particle migration	Effect of solids fraction in suspension	Effect of pressure on green bodies formed from dispersed suspensions	Effect of pressure on green bodies formed from flocculated suspensions	Effect of green microstructure on green density				Effect of particle size distribution on green density	
Suspension dispersion method		Commercial Deflocculent 'Darvan 7'		pH 4 by HNO ₃ /NH ₄ OH	pH by HCl/ NH ₄ OH	pH 2 by HCl	pH 3- 9 by HNO ₃ /NH ₃				Tetrasodium pyrophosphate	
Suspension flocculation method		Not applicable		Not applicable	pH by HCl/ NH ₄ OH	pH 8.5 by NH ₄ OH					Not applicable	
Fine powder	d ₅₀	0.4 µm	0.4 µm	0.3 µm	0.4 µm	0.4 µm	0.61 µm [#]	0.19 µm [#]	0.38 µm ^{††}	0.132 µm ^{††}	0.6 µm	
	d ₉₀	2 µm	2 µm	0.9 µm	1 µm	1 µm					3 µm	
Intermediate powder	d ₅₀										5 µm	
	d ₉₀										20 µm	
Coarse powder	d ₅₀	Not applicable	4 µm	1 µm	Not applicable						3 µm	
	d ₉₀	Not applicable	8 µm	2 µm	Not applicable						40 µm	
Mixture of fine and coarse powders	d ₅₀	Not applicable	?	0.9 µm	Not applicable							
	d ₉₀	Not applicable	?	1 µm	Not applicable							
	Percentage fines in mix	Not applicable	20 %	40 %	Not applicable							
Particle size determination method		X-ray sedimentation	X-ray sedimentation	X-ray sedimentation	Sedimentation?	Manufacturer claim	Stokes settling	N ₂ adsorption	Stokes settling	N ₂ adsorption	X-ray sedimentation	
Forming technique		Slip casting	Filter casting	Filter casting	Filter casting		Filter casting, centrifugal casting and dry pressing.				Filter casting	Slip casting

* The same powder characterised in two ways.

‡ The same powder characterised in two ways.

Broad size distribution powder.

† Narrow size distribution powder.