MANUFACTURING OF RIGID POROUS FILTERS

by

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ABSTRACT

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Filtration is a basic operation frequently used in ceramic industries. Ceramic articles can be shaped using appropriate molds with or without pressure application.

In this study, plastic molds with filter properties, high porosity and good permeability, are manufactured by using acrylic polymer powders. Furthermore the pore sizes hence permeability is adjusted by using different particle sizes of these powders. Also a porous open-pore, hardened plastic composition for low pressure slip casting process is manufactured by subjecting a water in oil emulsion to hardening.

Pressure slip casting process requires coarser pores while slip casting process requires fine pores like plaster. The achieved pore sizes are 20-40 μm for molds which can be used in high pressure slip casting and 3-5 μm for molds which can be used in low pressure slip casting.

ÖZET

RİJİT GÖZENEKLİ FİLTRELERİN ÜRETİMİ

Filtreleme işlemi seramik endüstrisinde sık kullanılan bir işlemdir. Seramik parçaların şekillendirilmesi uygun kalıplarla, basınç uygulayarak veya basınçsız yapılabilmektedir.

Bu çalışmada filtre özelliği gösteren yüksek gözenekli ve iyi geçirgenlikli plastik kalıpların akrilik polimer tozlarından üretimi gerçekleştirilmiştir. Ayrıca gözenek büyüklüğü dolayısıyla geçirgenlik çeşitli toz çapları kullanılarak kontrol edilmiştir. Aynı zamanda düşük basınçlı döküm işleminde kullanılabilecek, yağda emülsiye edilmiş su yöntemi ile sertleşen, gözenekli bir kalıp üretimi de gerçekleştirilmiştir.

Basınçlı çamur döküm işlemi kaba gözenek yapılı kalıplarla yapılırken pozitif basınç uygulanmayan döküm işlemi, alçı kalıplarda olduğu gibi, ince gözenekli kalıplarla yapılır. Elde edilen gözenek büyüklükleri yüksek basınçlı döküm işlemi için 20-40 mikrometre ve düşük basınçlı döküm işlemi için 3-5 mikrometre olmuştur.

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A	Area of the filter or mold
C	The volume fraction of solids
d	Plunger displacement
d_s	Particle diameter
J	Volume of cast per volume of liquid removed
k	Permeability
k_0	Shape factor
k_t	Tortuosity constant
K	Kozeny constant
L	The depth or thickness of the bed
P	Pressure drop
P_a	Pressure applied to the slurry
P_c	Capillary suction pressure
Q	Volumetric flow rate
Q_c	Constant rate of filtration
Q_f	Final rate of filtration
R_c	Resistance of the cake
R_m	Resistance of the mold
R_t	Arithmetic sum of individual resistances
S_v	Specific surface area for unit volume of particles
t	Filtration time
v_0	The volume fraction of solids in slurry
v_l	The volume fraction of solids in consolidated layer
V	Cumulative volume of filtrate collected in time t
w	Weight of dry cake per unit weight of dry solids
W_{wp}	water penetrated into the pores
α	Specific resistance to filtration per unit weight of dry solids
ΔP	Pressure difference across length L

ε	Porosity
γ	Contact angle
μ	Absolute viscosity
ρ_s	Density of the solids
ρ_{dw}	Density of distilled water
σ	Surface tension of water

1. INTRODUCTION

Rigid porous filters for clarification of liquids from impurities are used in a broad range of applications. Clarifiers specifically remove solid impurities from a single liquid phase. Here the product is the filtrate, clean liquid and particles retained at the filter surface are washed away or removed. In some cases however, the fluid is the carrier and the product is the retained particles which form a homogeneous cake at filter's surface. Slip casting for example is a filtration process, in which a powder suspension is poured into plaster mold. Porosity of the mold creates capillary forces and removes liquid from the suspension. Using pressure to accelerate the dewatering process improves the filtration rate hence the productivity.

Solids-liquid separation duty can be performed by basic mechanical filters. The filter element works as a porous screen, removing and retaining solid particles too large through the openings. Specifically the filter provides direct interception of such solids. This mechanism is the simplest type of mechanical filtration. Filter element most commonly used in slip casting is gypsum (generally referred to as plaster mold). Improved filter media such as porous polymers which combine high porosity, relatively high mechanical strength, and good elasticity are used for higher pressure applications. There will be a number of different types of filter which may be suitable for different applications, although specific applications commonly adopt certain types as the virtual standard on the basis of proven satisfactory performance, cost, availability, and other commercial considerations [1].

Control of the filtration process is based on four parameters; the pressure differential on the body, the liquid medium viscosity, the specific surface area of the slip's solids content and the body porosity (body formation is dependent on the permeability of the layer of body that has already formed from filtered material). The mechanics of slip casting and pressure slip casting is governed by the theory of cake filtration, that is the laws of flow through compressible, porous, particulate structures. The established

The size of the filter needs to be selected with regard to the acceptable pressure drop and life required between element replacement. This is closely bound up with the type of the element and medium employed. Plaster molds, used as filter media in slip casting, have an adequate porosity, fine pore structure, and simplicity in processing. However the short service life, low durability and relatively low filtration rate are the main disadvantages. Another drawback to the slip casting process has been the long setup time required by cast articles in the mold. Hence, a large quantity of molds was required to achieve commercial production rates, resulting in the use of large amounts of floor space and labor. Attempts have been made to achieve shorter shaping times in the slip casting process by the use of positive pressures. These technical developments have resulted in an alternative forming process which offers the intricate shape capabilities of slip casting while approaching the faster production rates of plaster forming. This alternative is pressure slip casting [2].

The pressure slip casting process is directly comparable to filter pressing with the basic difference being that the filter medium in the pressure casting machine must both filter and shape the end product [2]. It requires a filter medium, a porous mold material having a uniform open pore structure, good surface properties and adequate mechanical strength. Therefore plaster molds are not suitable for the pressure casting process. In the age of plastic there are materials which may be worked into molds simply and at low cost, preferably using the conventional methods for producing plaster molds. Methods for manufacturing porous plastic molds varies in terms of ingredients of the resin and processing techniques [3, 4]:

- Sintering of thermoplastic resin powder
- Pressing or stamping of mixtures of thermosetting resins and fillers
- A method compromising curing a resin solution containing a pore-forming agent through dissolution-extraction or evaporation
- A method which makes use of a blowing agent
- A method compromising curing and polymerizing a water in oil (w/o) type emulsion such as water-containing polyester resin or acrylic resin and then evaporating water

- A method comprising curing a oil in water (o/w) type emulsion such as mixture of a glycidyl-type epoxy resin, polymeric fatty acid polyamide hardener, filler and water.

In pressure slip casting pressures up to 4 MPa can be used. The plastic molds manufactured are able to operate successfully under these high-pressure casting conditions [2].

Plaster and porous plastic molds are basically filters which recover the solid (green ceramic product) and filtrates water. Hence knowledge in filtration is essential to understand the effect of molds in slip casting and pressure slip casting processes.

The purpose of this thesis is to manufacture molds with plastic materials. Also the effects of the ingredients physical properties to the resultant product will be analyzed. The control of pore sizes and pore volume, hence permeability of the molds is important. Image processing techniques and laboratory permeability analysis will be conducted in order to make comparisons between the molds manufactured.

2. FILTERS AND FILTRATION

A filter is basically a device for separating one substance from another [1]. This general definition covers an extremely wide variety of industrial equipment, the performance of which is dependent upon many different parameters. The latter include not only the driving force (gravity, vacuum, pressure or centrifugal), but also the nature of the filter medium (e.g., cloth, paper, sintered metal, sintered plastic, etc.,) and also the type of pretreatment to which the solid/liquid suspension may have been subjected before filtration (e.g., temperature changes, adjustment of pH, addition of flocculants, etc.) [5].

The characteristics of the solid/liquid suspension to be processed influence profoundly the suitability of a given type of filter for a specific duty. The practical choice of filter for a specific application is generally based on a combination of the suitability of the basic type, the determination of the necessary size, and an assessment of the likely capital and operating costs. Estimating the size is often much more difficult, since it generally requires knowledge of filtration rate data [5].

An understanding of the fundamental mechanisms of filtration can be of great value, both qualitatively and especially quantitatively.

2.1. Filtration Mechanisms

Whereas in practice it is common for two or more filtration mechanisms to occur either simultaneously or in very rapid succession, it is convenient to distinguish between four basic types, which are *surface straining*, *depth straining*, *depth filtration* and *cake filtration* [5].

Surface Straining involves the deposition of solid particles on the outer (upstream) surface of the medium. As shown in Figure 2.1, it will occur provided the particles are larger than the pores of the medium; smaller particles pass through the

medium and remain in the filtrate. This is the operating mode of a plain weave mesh made from a monofilament of plastic or metal wire [5].
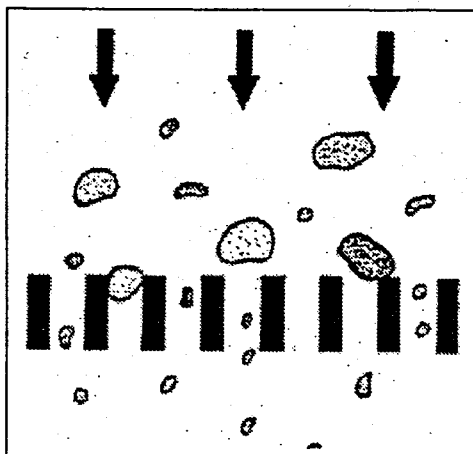
Figure 2.1. Surface straining mechanisms [5]

Depth Straining resembles surface straining but recognizes that with certain media, the cross-sectional area of a pore may be less within the depth of the medium than at the surface. With such a pore, a particle may be small enough to escape being trapped on the surface but is then caught by the same mechanism of straining at some point within the depth of the medium, as illustrated in Figure 2.2. This is the operating mode of felts and of cellulose ester membranes.
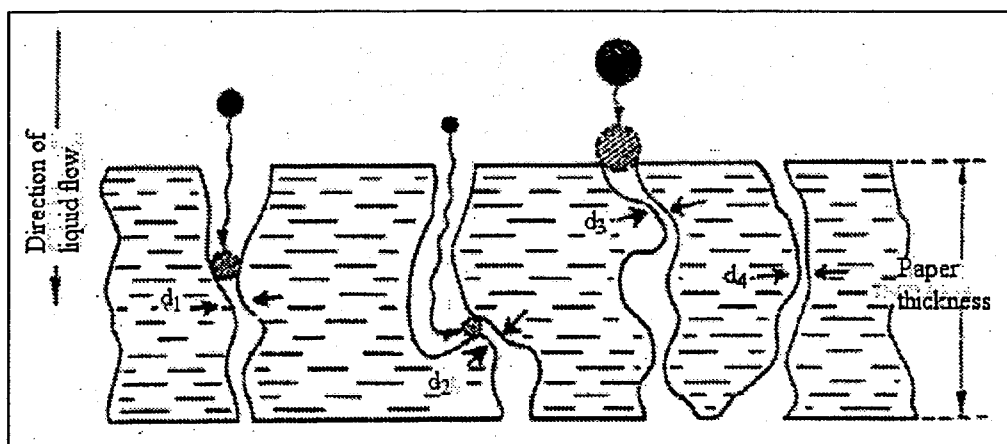
Figure 2.2. Depth straining mechanisms [5]

Depth Filtration is the mechanism whereby, even though the particles are very much smaller than the pores of the medium, they are nonetheless trapped in the depth of the medium as the liquid flows through it. More strictly, depth filtration is a combination of mechanisms rather than a single mechanism, the overall result being that the solid particles adhere either to the internal surfaces of the medium or to each other, as in Figure 2.3. This is the operating mode of filter sheets (e.g., cellulose/asbestos) and also of deep bed filters (e.g., sand).
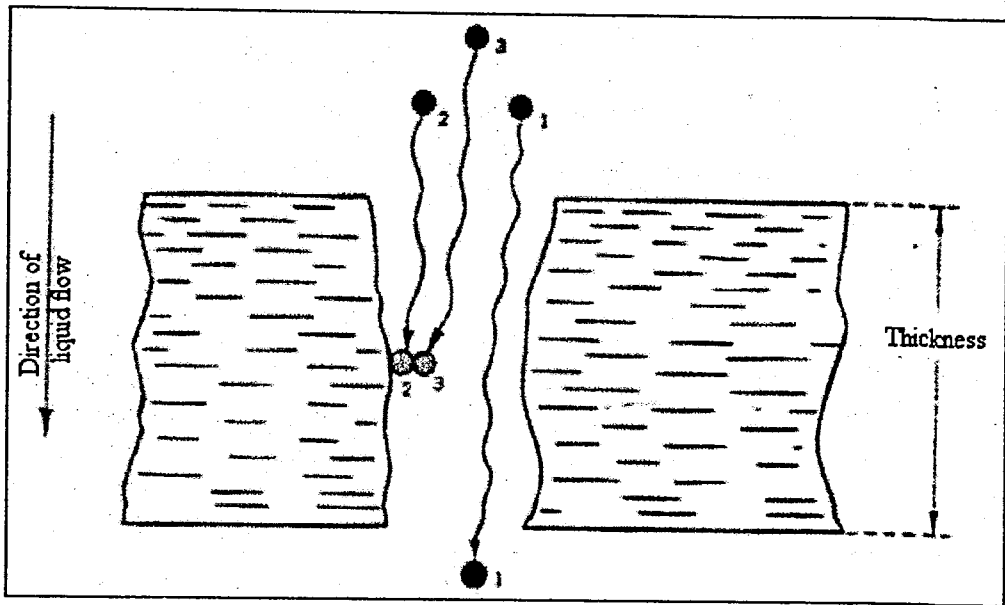
Figure 2.3. Depth filtration mechanisms [5]
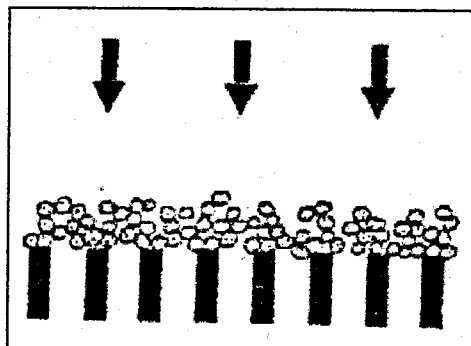
Figure 2.4. Cake filtration mechanism [5]

Cake Filtration describes the accumulation of a thick layer of particles on the surface of the medium, as illustrated in Figure 2.4. If the solid particles are larger than the pores, then cake filtration is preceded by a period of surface and/or depth

straining. Frequently, however, the particles are substantially smaller than the pores; cake filtration is then preceded by a bridging process, as in Figure 2.4. Cake filtration is the general mode of operation whenever solids are being recovered (i.e., as opposed to clarification).

Bridging, as a preliminary to cake filtration, cannot occur if the concentration of solids in the suspension is too low, or if the particles are too small in comparison with the size of the pores in the medium.

The relevance of these four filtration mechanisms to applications involving solids recovery on the one hand and clarification on the other hand is summarized in Table 2.1; the symbol x denotes a major mechanism, while (x) denotes a minor mechanism [5].

Table 2.1. Filtration mechanisms and practical applications [5]

MECHANISM	APPLICATION	
	SOLIDS RECOVERY	CLARIFICATION
1. Self straining	(x)	x
2. Depth straining		x
3. Depth filtration		x
4. Cake filtration	x	(x)

2.2. Filtration Theory

Common to all filtration mechanisms, is the flow of liquid through porous medium. The distinctive feature of filtration is that solid particles suspended in the liquid are retained on the surface or in the depth of the medium.

The process needs a driving force (e.g., pressure) to overcome the resistance both of the medium itself and of the solid particles after they have been deposited. With a

clean liquid containing no particles, the resistance of the system does not change with time, so that with a constant driving force the flow rate remains constant. By contrast, the presence of particles in the liquid results in filtration, in the progressive increase in resistance of the system, and in a decline in flow rate at constant driving force.

The fundamental relation between the pressure drop and the flow rate of liquid passing through a packed bed of solids, such as that shown in Figure 2.5, was first reported by Darcy in 1856. The liquid passes through the open space between the particles, i.e. the pores or voids within the bed. As it flows over the surface of the solid packing frictional losses lead to a pressure drop.

The amount of solids inside the bed is clearly important; the greater this is the larger will be the surface over which liquid flows and, therefore, the higher the pressure drop will be as a result of friction. The volume available for fluid flow is called the porosity [6].

$$\text{Porosity} \; = \; \varepsilon \; = \; \frac{\text{volume of voids}}{\text{total bed volume}} \tag{2.1}$$

In many solid-liquid separation the use of solid concentration is often preferred to porosity. This is usually the volume fraction of solids present within the bed C; porosity is the void volume fraction so these fractions sum to unity [6]:

$$\begin{array}{ccccc} \text{void fraction} & + & \text{solid fraction} & = & \text{unity} \\ \varepsilon & + & C & = & 1 \end{array} \tag{2.2}$$

Hence solid volume fraction concentration is:

$$C \; = \; 1 \; - \; \varepsilon \tag{2.3}$$
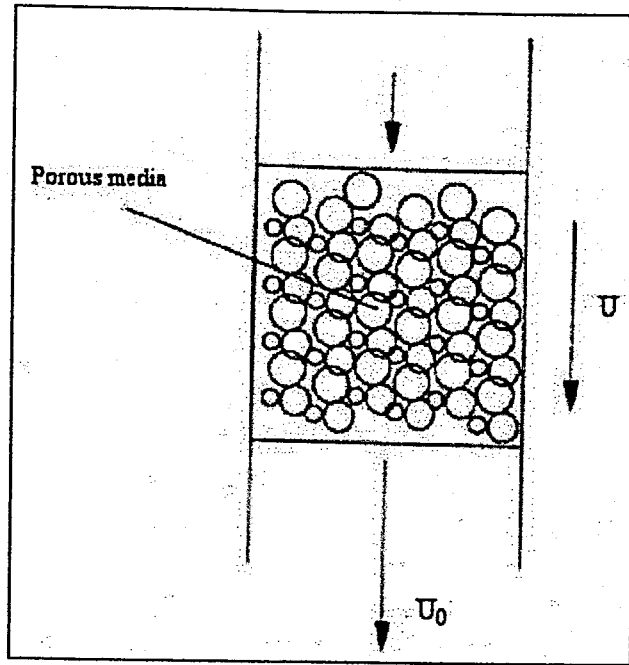
Figure 2.5. Schematic diagram of porous media [6]

Darcy discovered that the pressure loss was directly proportional to the flow rate of the fluid. This is shown in Figure 2.6. The mathematical description of the process starts with the neglect of septum resistance and the use of Darcy's law (Equation (2.4)) to relate filtrate flow rate and pressure drop:

$$\frac{\Delta P}{L} = \frac{\mu}{k}\frac{dV}{dt}\frac{1}{A} \tag{2.4}$$

The constant of proportionality in the figure is dependent on the permeability k of the porous network. The flow of clean liquid through a porous medium can be described by the modified Darcy equation [5]:

$$\frac{Q}{A} = \frac{P\,k}{L\,\mu} = \frac{P}{R_m\,\mu} \tag{2.5}$$

where P is the pressure drop, L is the thickness, Q is the volumetric rate of flow, μ is the viscosity of the fluid, A is the area of the filter, R_m is the resistance of the medium, and k is its permeability. The deposition of solids on a filter medium or septum is shown schematically in Figure 2.4.
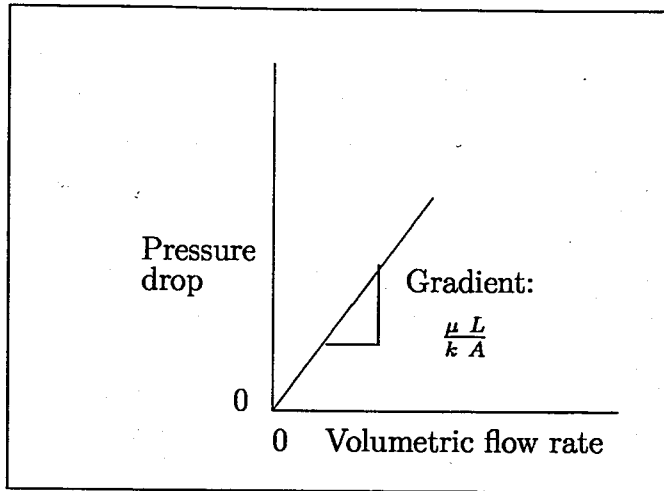
Figure 2.6. Proportional relation between pressure drop and flow rates clean liquid flowing through fixed porous media [6]

The permeability characterizes the ease with which liquid will flow within a porous medium, including filter cakes. Factors which affect permeability include the size of particles making up the porous medium and the porosity. The best known equation for permeability is due to Kozeny [6]:

$$k = \frac{\varepsilon^3}{K (1-\varepsilon)^2 S_v^2}$$ (2.6)

where S_v is the specific surface area per unit volume of the particles, K is the Kozeny constant which normally takes the value of 5 in fixed or slow moving beds and 3.36 in setting or rapidly moving beds. The specific surface area is discussed in greater detail elsewhere [6]. Substituting Equation (2.6) into Darcy's law gives the Kozeny-Carman equation [6]:

$$\frac{\Delta P}{L} = \mu \, \frac{5 \, (1-\varepsilon)^2 \, S_v^2}{\varepsilon^3} \, \frac{dV}{dt} \, \frac{1}{A}$$ (2.7)

In the permeability models the particles are assumed to be rigid, in a fixed geometry and in point contact with each other. Furthermore, liquid drag and pressure were

the only forces considered. Thus any other body force present could cause deviation from the above simplified approach. Such forces are generally significant for particles less than 10 μm, care should be exercised when applying these relations to material less than this size [6].

In filtration it is usually possible to deduce an empirical permeability from simple laboratory tests or from existing operating data. In practice filter cake permeability is a function of porosity, particle shape and packing , particle size and distribution, rate at which the cake was formed, concentration of the slurry being filtered, etc. Thus the theoretical relations for permeability should be used only as a guide to estimate permeability in the absence of operating data; measured permeabilities may easily be one or two orders of magnitude lower than that given by the above equations. This is also a consequence of the many factors that the above equations do not recognize. It is also generally true that the finer the particles, and the wider the size distribution, the greater will be the deviation from the theoretical permeability relation [6].

The relationship in Equation (2.5) assumes that the flow regime is streamlined and not turbulent. While this assumption is almost always true so far as the filter medium is concerned, it may in practice be obscured by turbulent flow in the inlet and outlet ducts and piping which form part of the filter itself. As a consequence, whereas doubling the pressure drop across the medium alone would double the flow rate, the practical effect of doubling the pressure drop across a filter may be substantially less advantageous [5].

Where filtration is occurring, Equation (2.5) must be modified to include the resistance of the deposited solids. This resistance increases progressively with time at a rate which depends upon the type of filtration mechanism, typically being much less with depth filtration than with cake filtration. Partly because of this, and also because of its dominance in the progressing industry, a consideration of filtration theory is frequently limited to the cake mechanism; a further factor is no doubt the ease with which the elementary cake theory can be understood and put to practical use [5].

The general cake filtration equation may be written in the form [5]:

$$\frac{Q}{A} = \frac{1}{A} \cdot \frac{dV}{dt} = \frac{P}{\mu\left(\frac{\alpha w V}{A} + R_m\right)}$$ (2.8)

where V is the cumulative volume of filtrate collected in time t, α is the specific resistance to filtration per unit weight of the dry solids deposited as a cake, and w is the weight of dry cake per unit volume of filtrate. This equation states the instantaneous conditions at any moment during filtration and can be integrated over a finite time interval for either constant pressure or constant rate filtration.

For *constant pressure filtration*, the only variables are flow rate and total filtrate. The above equation may therefore be simplified to give [5]:

$$\frac{1}{Q} = \frac{dt}{dV} = V\left(\frac{\mu \alpha w}{A^2 P}\right) + \left(\frac{\mu R_m}{AP}\right)$$ (2.9)

which may be written in the abbreviated form [5]:

$$\frac{1}{Q} = \frac{dt}{dV} = aV + b$$ (2.10)

in which a and b are constants. Simple manipulation of this equation makes it possible to calculate the total volume of filtrate when the rate of filtration has fallen to a final level, Q_f, after a time t.

Rearrangement of Equation (2.10) permits V to be evaluated from Equation (2.11), while integration of Equation (2.10) gives t from Equation (2.12):

$$V = \frac{1 - bQ_f}{aQ_f}$$ (2.11)

$$t = \left(\frac{a}{2}\right)V^2 + bV$$ (2.12)

For *constant rate filtration*, the variables are pressure and the total volume filtered, so that Equation (2.9) may conveniently be arranged in the form [5]:

$$P = \frac{\mu \alpha w Q_c}{A^2} \cdot V + \frac{\mu R Q_c}{A} \tag{2.13}$$

This gives directly the final pressure required to permit collection of a total filtrate volume V at constant rate, Q_c. The time required, t, is given by the separate simple Equation (2.14):

$$t = \frac{V}{Q_c} \tag{2.14}$$

2.3. Selection of the Filter Medium

Advances in plastics and fibre technology have made available an extensive of materials, and filter media can be found to meet almost all requirements, such as corrosion resistance, filtrate clarity, ease of cake discharge and freedom from blinding. Table 2.2 presents a convenient and highly condensed summary of the immense variety of filter media available for liquid filtration [7]. In this table, media have been arranged in the order of decreasing rigidity, primarily as an arbitrary device to impose a degree of order on this confusing field; in practise, rigidity is an important criterion controlling the suitability of a given medium for use with a specific type of filter.

With so wide a choice of filter media, selecting the right one for a specific application can be a source of great difficulty. Account must be taken of many different properties which for convenience may be divided into three broad categories [7]:

- *machine-oriented properties*, which restrict the use of a medium to specific types of filter (its rigidity, strength, ability to be fabricated, etc);
- *application-oriented properties*, which control the compatibility of a medium with the process environment (its chemical and thermal stability, etc);

Table 2.2. Generalized summary of filter media on basis of rigidity [7]

MAIN TYPE	SUBDIVISIONS
1. Solid fabrications	(a) Bar screens
	(b) Wire-wound tubes
	(c) Stacks of rings
2. Rigid porous media	(a) Ceramics and stoneware
	(b) Plastics
	(c) Carbon
	(d) Sintered metals
3. Cartridges	(a) Sheet fabrications
	(b) Yarn wound
	(c) Bonded beds
4. Metal sheets	(a) Perforated
	(b) Woven wire
5. Plastic sheets	(a) Woven monofilament
	(b) Porous sheets
	(c) Membranes
6. Woven fabrics	(a) Monofilament
	(b) Multifilaments
	(c) Staple fiber yarns
7. Nonwoven media	(a) Filter sheets
	(b) Felts and needle felts
	(c) Paper media
	-cellulose
	-glass
	(d) Polymeric nonwovens (melt blown, spun bonded, etc)
8. Loose media	(a) Fibers
	(b) Powders
9. Membranes	(a) Ceramic
	(b) Metal
	(c) Polymeric

- *filtration-specific properties*, which determine the ability of a medium to achieve a specified filtration task(its efficiency in retaining particles of a defined size, resistance to flow, etc).

The individual properties in each category are summarized in Table 2.3, Table 2.4, and Table 2.5. Of these three groups of properties, the filtration-specific one listed in Table 2.5 presents the greatest difficulty, because of a simultaneous lack of data combined with a frequent ambiguity of such data as is available [7].

Table 2.3. Machine-oriented properties of filter media [7]

1.	Rigidity
2.	Strength
3.	Resistance to creep/stretch
4.	Stability of edges
5.	Resistance to abrasion
6.	Stability to vibration
7.	Dimensions of available supplies
8.	Ability to be fabricated
9.	Sealing/gasketing function

The final choice of the optimum filter medium for a specific application should obviously also take account of cost factors. This is a complex topic, which to receive the attention which it merits, requires a comprehensive study of the total annual costs of each alternative scheme under consideration; on this basis, it by no means follows that the cheapest medium per unit area is the appropriate choice.

A good filter medium, depending on the specific problem should;

- be able to retain a wide size distribution of solid particles from the suspension,
- offer minimum hydraulic resistance to the filtrate flow,
- allow easy discharge of cake,

Table 2.4. Application-oriented properties of filter media [7]

1.	Chemical stability
2.	Thermal stability
3.	Biological stability
4.	Dynamic stability
5.	Absorptive characteristics
6.	Adsorptive characteristics
7.	Wettability
8.	Health and safety aspects
9.	Static characteristics
10.	Disposability
11.	Suitability for re-use
12.	Cost

Table 2.5. Filtration-specific properties of filter media [7]

1.	Smallest particle retained
2.	Retention efficiency
3.	Resistance to flow
4.	Dirt-holding capacity
5.	Tendency to blind
6.	Cake discharge characteristics

- be resistant to chemical attack,
- not undergo swelling when in contact with filtrate and washing liquid,
- be heat-resistant within the temperature ranges of filtration,
- have sufficient strength to withstand filtering pressure and mechanical wear,
- be capable of avoiding wedging of particles into its pores.

2.4. Testing Filter Media

A part from mechanical strength, the properties of filter media of particular interest are the five "filtration-specific properties" identified in Table 2.5, namely:

1. the smallest particle the medium is able to retain,

2. the efficiency with which particles of a defined size are retained,

3. the resistance of the medium to the flow of clean fluid through it,

4. the dirt holding capacity of the medium,

5. the tendency of the medium to blind, especially when used repeatedly in an operating cycle which includes cleaning (e.g. due to particles adhering tenaciously to the medium).

A large and ever increasing number of standard tests are available for characterizing filters or media. Test procedures designed to characterize a medium in respect of these properties involve challenging the medium either with a suitable clean fluid, or with fluid containing dispersed particles of selected and controlled characteristics.

Challenging with a clean liquid permits evaluation of:

• the permeability or resistance to flow per unit area of medium, such as the flow rate of air and water under a defined pressure,

• the size of the pores of the medium, in terms of the ideal cylindrical pores, hence an approximation of the size of particle the medium can retain by straining mechanisms.

2.4.1. Permeability

Permeability is the reciprocal expression of the resistance to flow offered by a filter. Thus high permeability represents low resistance, and low permeability high resistance. It is normally expressed in terms of *permeability* (k) related to pressure

drop (P) at a given flow rate (Q):

$$k = \frac{Q \, \mu \, L}{P \, A}$$

(2.15)

where A, L and μ are filter surface area, the depth or thickness of the bed, and viscosity of the fluid. Suitable permeability measurements can be made with apparatus of varying degrees of sophistication.

2.4.2. Pore Size

Pore size analysis are made for various types of pore which may occur in a porous material. Those which are relevant to filtration are identified as "through pores". The four most commonly used methods for measuring the pores of porous materials are briefly summarized below [7].

Bubble point testing, known also as liquid expulsion testing, utilises a controlled air pressure to empty open through pores filled with a wetting liquid. A simple relationship between the pressure, the properties of the liquid and the diameter of an ideal circular pore, permits calculation of equivalent pore diameter. The largest pore size, mean flow pore size, which is the flow distribution based on the pore diameter, and the permeability are measured. Only the active or through pores (pores that contribute to the flow) are detected by this technique. The dead-end or blind pores, i.e. pores that start from the surface and terminate inside the material, are not characterized. This method is normally used for pore size range 0.005 to 100 μm [7].

Mercury porosimetry, known also as mercury intrusion, involves filling the pores with mercury under pressure up to 400 MPa. The volume of mercury forced in, which can be measured very accurately, is related to pore size and pressure by the same relationship used in the bubble point test. It is classified as non-wetting process. The intrusion volume is recorded as a function of the pressure, and the pore size information is calculated from the pressure and the intrusion volume. In contrast to the bubble point test, this technique also detects the blind, as well as the through pores. Thus

the total pore volume, surface area and pore size distribution based on volume can be calculated. This method is suitable for many materials with pores in the size range 0.003 to 400 μm, and especially in the range 0.1 to 100 μm [7].

Gas adsorption, typically involves measuring the quantity of nitrogen absorbed as its relative pressure is progressively increased at a constant cyrogenic temperature. This is a well-known technique used to determine the surface area of the porous materials. The amount of a gas adsorbed on the material under increasing relative pressure at a constant temperature is monitored and used to calculate pore characteristics . Once the amount of adsorbed gas, which corresponds to the monolayer coverage, is estimated the total surface area of the material can be calculated from the effective cross sectional area of the adsorbate molecule. This technique also detects both the flow-through and blind pores. The minimum size of pore which can be studied is restricted by the 0.4 nm size nitrogen molecule; the maximum is limited to about 50 nm by the practical difficulty of measuring the amount of nitrogen adsorbed at high relative pressure. The method is therefore is most appropriate for pores in the size range 0.0004 to 0.04 μm [7].

Challenge tests determine the effective size of open pores by challenging them with suspensions of particle of known sizes. This method is particularly used for pores in the size range 0.005 to 100 μm [7].

3. MANUFACTURING PROCESSES BASED ON FILTRATION PRINCIPLES

3.1. Slip Casting

Casting processes begin by filling a mold with a ceramic slurry having a pourable consistency. The cast is produced when a physical, chemical, and/or thermal change causes the slurry to develop a yield strength. There are two types of slip casting:

- Drain casting.
- Solid casting.

In drain casting, the cast forms adjacent to the mold surface, and after the wall has grown to the desired thickness, excess slurry is drained from the mold. Solid casting produces a solid cast having the shape of the cavity of the mold. The cast may or may not be dried before it is removed from the mold.

An aqueous slurry containing fine clay is called a slip. Slip casting is the conventional casting of a slip or a slurry in a porous gypsum mold. Capillary suction of water into the mold concentrates and coagulates the particles in the slip near the mold surface, forming the cast. Pressure applied to the slurry (Section 3.2), a vacuum applied to the mold (vacuum-assisted casting), or centrifuging (centrifugal casting) may be used to increase the casting rate [8].

Drain casting and solid casting are used to produce a variety of traditional porcelain products such as fine china and dinnerware and industrial porcelain components. Slip casting processes are used to make dense refractories that are of a complex shape, thin walled products such as crucibles and closed-end tubes, and structural refractories that are large in cross section. Coarse grained structural refractories and concrete products are widely produced by solid casting. The advantages of casting processes are the more complete powder dispersion in a relatively low-viscosity liquid, the complexity

of product shape permissible, and the relatively low capital cost. The disadvantages of casting are the lower production rates and lower dimensional precision commonly obtained.

3.1.1. Preparation of the Slurry, Slip Rheology

The formation of a cast by drain casting and solid casting is shown in Figure 3.1. Steps involved in the slip casting process are the preparation of the slurry, beneficiation of the slurry by screening or some other form of classification and evacuation of air, mold filling, casting, draining, partial drying while in the mold, separation from the mold, and sometimes trimming and surface finishing before the final drying [8].
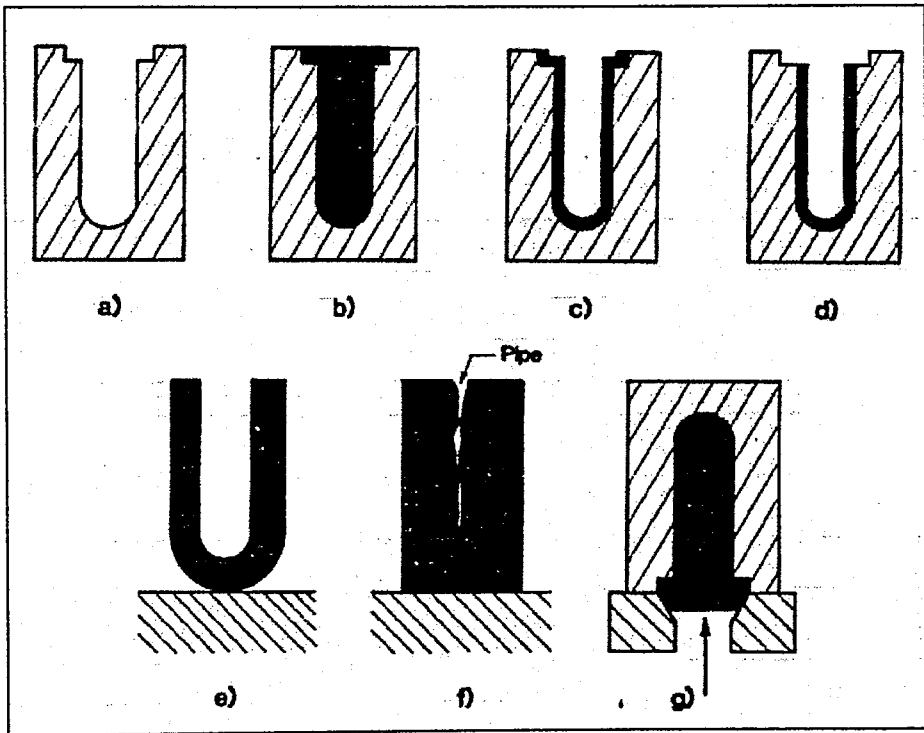
Figure 3.1. Drain casting (a-e), solid casting (f) and pressure casting (g) [8]

In drain casting as shown in Figure 3.1, (a) a porous mold is (b) filled with slurry; after a period of casting (c) excess slurry is drained form the mold leaving a hollow cast which (d) may be trimmed in place if of sufficient strength and toughness. A longer casting time will produce a cast having (e) a thicker wall and when continued

(f) a nearly solid cast is formed. In (g) pressure casting, the slurry is pressurized and pumped into the mold

Figure 3.2 presents a processing flow diagram for a well-controlled slip casting process. Ideally the behavior of the casting slurry should not be sensitive to slight variations in chemical composition or particle size distribution [8]. The viscosity must be low enough to allow complete filling of the mold, but the solids content must be high enough to achieve a reasonable casting rate. Empirical methods are traditionally used to determine optimum conditions. The slip must also be free of air bubbles (or chemical reactions producing bubbles) that may become critical defects in the sintered part [9]. The slurry should have a reasonable storage life and aging may be required to obtain a time-stable slurry. The final viscosity measurements are performed before deairing and casting.

Control parameters are the proportions and dispersion of components in the slurry, slurry rheology during mold filling the casting rate, the density and yield strength of the cast, flow rheology on draining, shrinkage and release of the cast from the mold, the strength and mechanical toughness of the product removed from the mold, and trimming and surface finishing.

Slurries containing liquids, solids, and processing additives (Table 3.1) may be prepared in a variety of mixers and in ball mills, planetary ball mills, and vibratory mills [8]. Batch size may range from a fraction of a liter for a special ceramic to several thousand gallons when casting porcelain products. Intensive mixing and milling disperse agglomerates more completely and shorten the mixing time; however, low-intensity mixing for a longer time is used when solid materials can be comminuted in mixing and the proportion of submicron sizes must be relatively low. Additives that can degrade during mixing, such as binders of medium to high molecular weight, are often added near the end of the mixing cycle, and their potential degradation may influence the choice of mixing operation. Casting slips containing up to 50 per cent clay are often blunged for 8-48 hours to produce an "aged" time-stable slip with a reproducible casting behavior The mixing time is reduced when the clay is received
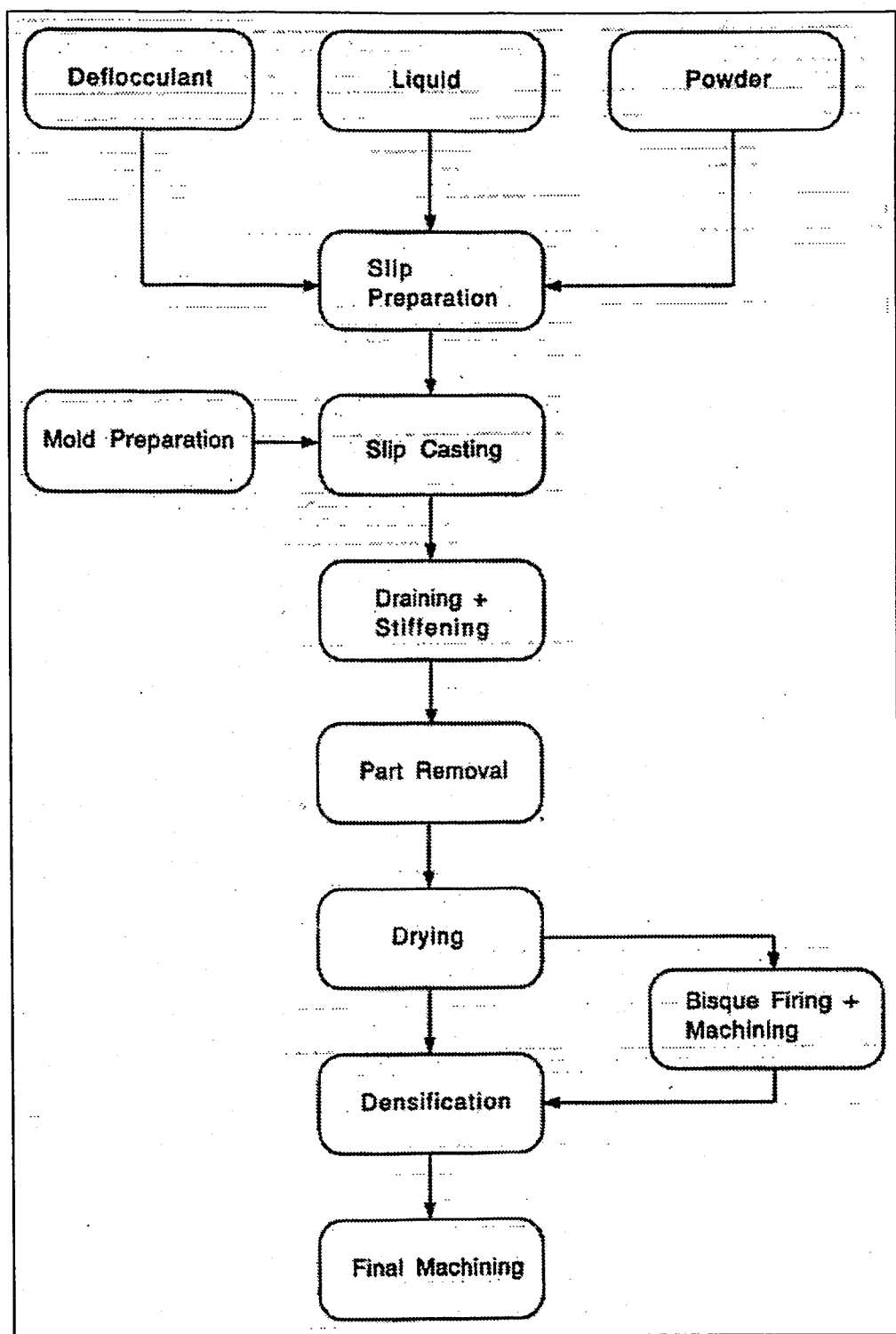
Figure 3.2. Flow diagram for the slip casting process [8]

as an aged slurry. Postmixing processes include classification, separation of magnetic material, temperature control, and deairing. A mixed slip may be conveyed in the mixing container or pumped into portable holding tanks for distribution.

Table 3.1. Compositions for Casting [8]

| Material | Concentration (vol. %) | |
	Porcelain	Alumina
Alumina		40-50
Silica	10-15	
	10-15	
	15-25	
	45-60	50-60
	100 vol. %	100 vol. %
Processing additives (*wt.%*[a])		
Deflocculant		
Na silicate		
NH_4 silicate	< 0.5	
NH_4 polyacrylate		0.5-2
Na citrate		0.0-0.5
Coagulant		
$CaCO_3$	< 0.1	
$BaCO_3$	< 0.1	
Binder		
Na carboxymethylcellulose		0.0-0.5
[a]Based on weight of solids in slurry.		

Proper control and characterization of slip rheology is perhaps the most important parameter in slip casting. Rheological properties are not only dependent on interparticle forces but also depend strongly on the particle size and concentration. In general, the viscosity increases with smaller particles and higher solids concentrations because of increased particle-particle interactions. For the same reason reduced viscosities generally result at a given solids concentration when spherical particles are used instead of platelets or rods.

Characterization of slips generally entails measurements of shear stress and viscosity as a function of shear rate over a range of shear rates of 1 to 10 s^{-1}. An important aspect of dense-packed colloidal structures in slip-cast layers is the ability to store and dissipate energy upon deformation (viscoelasticity). A full characterization of dense-packed networks can be obtained using experimental procedures such as stress growth forced oscillation, stress relaxation, or creep compliance [9].

Casting slurries are typically formulated to be shear thinning and have an apparent viscosity below 2000 $mPa \cdot s$ at a mold-filling shear rate of 1-10 s^{-1}, as shown in Figure 3.3. This viscosity behavior is convenient for mixing and pumping, and for flow when the mold is filled. A lower viscosity below about 1000 $mPa \cdot s$ is required when the slurry is screened and air bubbles must be quickly eliminated from the slurry [8].

The density and apparent viscosity or yield stress of the slurry should be high enough to minimize particle settling during casting.

Permeable molds for casting are commonly gypsum with 40-50 per cent porosity and an effective pore size of 1 to 5 μm. The casting time may range from a few minutes for a thin cast from a partially coagulated porcelain slurry to about 1 hour for a thick porcelain cast or a thin, dense cast from a well-deflocculated slurry of a powder containing submicron particles. The casting time for a dense solid cast refractory of fine particle size may range up to several weeks for thicknesses of 30 cm [8].

Once casting is completed a given part begins to dry and shrink away from the mold. This shrinkage is necessary to release the part from the mold. If sticking occurs the part can be damaged and rejected. Mold release can be aided by coating the walls of the mold with a release agent such as silicone oil, olive oil, or a dilute aqueous solution (5 weight per cent of sodium alginate). However, these coatings may alter the casting rate [9].
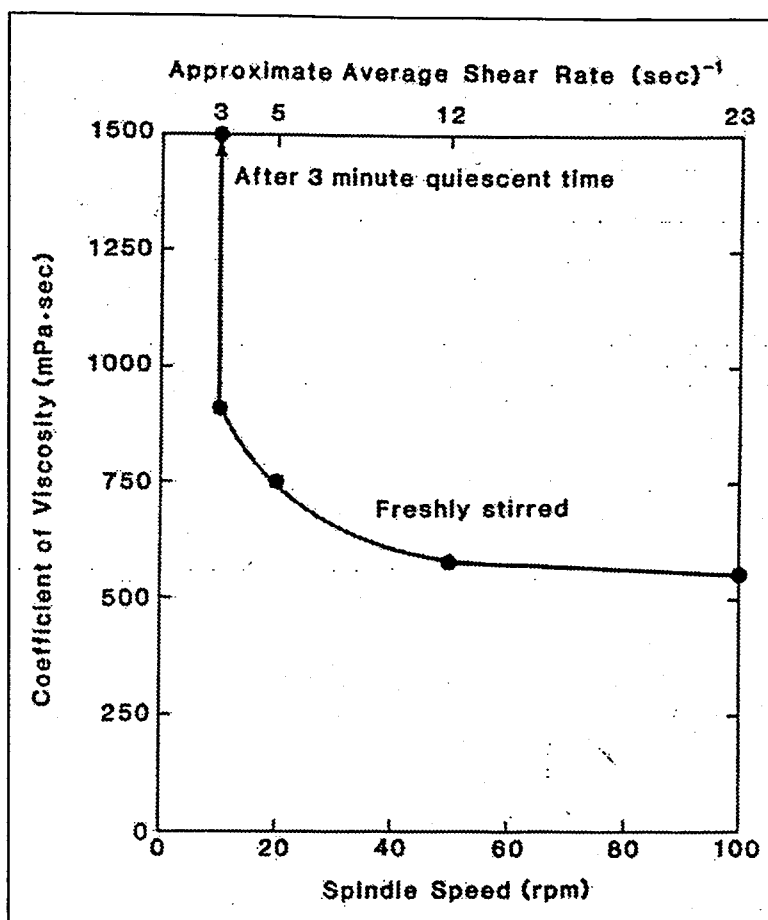
Figure 3.3. Porcelain slip for casting is shear thinning; gelation when at rest after

pouring causes the apparent viscosity to increase (53 volume per cent

solids in slip) [8]

3.1.2. Mechanics of Slip Casting

Solid-liquid separation is a basic operation frequently seen in the chemical process and ceramic industries. Slip casting is one of the solid-liquid separation operation encountered in the ceramic field. The theory of these operations is governed by the laws of flow through compressible, porous, particulate structures. In general, Darcy's law with variable permeability, material balances, constitutive relations relating porosity, permeability, and effective pressure, force balances, and boundary conditions imposed by the flow-actuating mechanism (capillary pressure) are necessary to developing theoretical formulas [10].

In slip casting, a mold (plaster of Paris) is made from gypsum for repetitive use. The porous structure of the mold provides a suction pressure ranging from 0.1 to 0.2 MPa. When slip is poured into the mold, water is sucked out by the capillarity leaving a layer of cake on the slip-mold interface. After drying and sintering, the final product is obtained [10].

The pressure at the gypsum-cast boundary is approximately equal to the capillary suction pressure, P_c, and is approximated by the Laplace equation:

$$P_c = S_v \sigma cos\gamma$$

where S_v is the specific surface area of gypsum, σ is the surface tension of water, and γ is the contact angle ($cos\gamma=1$ as gypsum is completely wetted by water) [9].

Slip casting is generally limited to the production of thin-walled articles (≈ 15 mm maximum thickness) because of casting rate limitations imposed by the hydraulic resistances of the cast and mold. The effects of process parameters on casting rates are revealed using a filtration kinetics model, which is based on an incompressible cake having a uniform cross-sectional area.

The consolidated layer of particles formed on the mold surface occurs by the process of filtration. For uniaxial filtration, the cast thickness L as a function of casting time t is [8]:

$$L = \left[\left(\frac{2J\Delta Pt}{\mu R_c} \right) + \left(\frac{R_m}{R_c} \right)^2 \right]^{0.5} - \left(\frac{R_m}{R_c} \right) \tag{3.1}$$

where J=volume of cast/volume of liquid removed, R_c is the resistivity to liquid transport in the cast, ΔP is the apparent mold suction, μ is the viscosity of the liquid transported, and R_m is the liquid transport resistance of the mold. Derivation of this equation is shown in Section 3.2.2. When the slip "ages" during casting, changes in the interparticle forces may cause a change in the particle packing and, therewith, J

and R_c. Commonly the ratio R_m/R_c is small, and the simplified equation [8]:

$$L = \left[\frac{2J\Delta Pt}{\mu R_c}\right]^{0.5}$$ (3.2)

approximates the behavior, as shown in Figure 3.4. The parameter $R_c = 1/k$, where k is the liquid permeability of the cast (k was described in Chapter 2). Equation (3.2) describes the casting when the liquid transport through the cast is rate limiting, which is the case when the porosity $\times$ (pore size)^2 is smaller for the cast than for the mold.
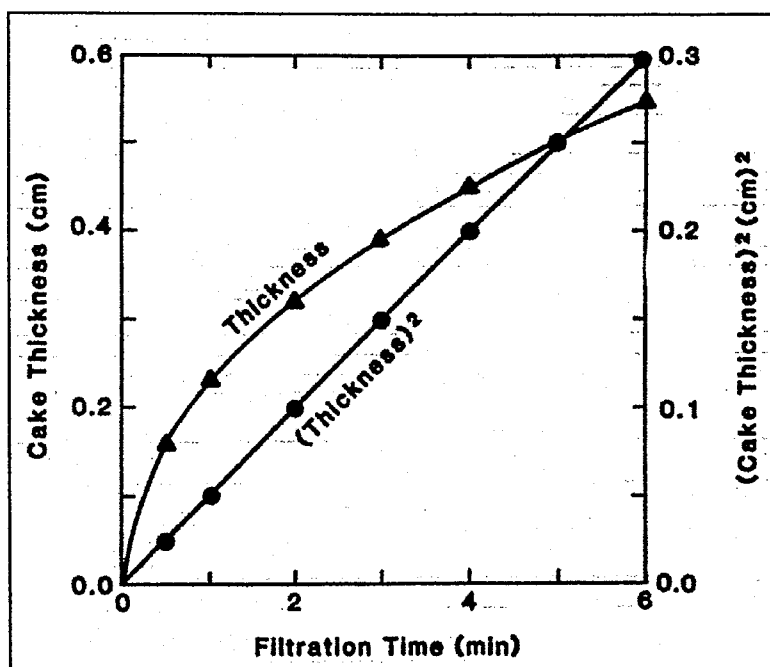
Figure 3.4. Parabolic behavior of cast thickness with time and linear dependence of cast (thickness) with time when slip casting a porcelain slip [8]

The transport of liquid in the mold due to capillary suction depends on the residual liquid in the mold and the depth of liquid penetration. The mold may become rate limiting after it has absorbed liquid from several casts, and the mold is said to be "waterlogged". Parameter adjustments to increase the casting rate are indicated by Equation (3.2). The parameter J is higher when the difference in liquid concentration between the slurry and the cast is small. A higher solids loading in the slurry will increase J. Heating the slurry may reduce the viscosity of the liquid, but heating may

also change the state of deflocculation which would change R_c [8].

Capillary suction of the mold depends upon the pore size distribution. As the pore size decreases, the capillary suction increases; but at the same time, the flow resistance increases. For each slip, there is an optimum pore size of the mold which produces a maximum rate of buildup of the consolidated layer [10].

In a recent study Zhang [11], discussed the effects of dynamic heating to the casting rate in slip casting. Casting rate can be increased at higher casting temperature as seen in Equation (3.2). Zhang found that a sustained high casting rate could be achieved by dynamic heating with pulse microwave energy. Water movement through the mold depended on the heating source and it was found that pulse microwave heating removed water from the slip more efficiently. Pulse microwave heating produced a better green body for handling and there were no significant differences in microstructures for green bodies cast. It was also seen that due to the pulsed nature (on-off cycles) of the microwave energy used, a low pressure phase had been created within the mold, most possible at the inner part of the mold due to the vaporisation and condensation of water and hence, the water would move dynamically within the mold. The vaporisation-condensation cycles would result in a high-pressure and a low-pressure short period leading to faster movement of water within the mold, higher casting rate and better green body [11].

Quality and strength of the final product depend on the microstructure of the cake. Highly porous cakes formed by a flocculated slip will usually shrink unevenly when sintered, resulting in crack like defects and reduced strength. Dispersed slips result in less particle aggregation and better structural uniformity. In general, aggregated slurries lead to compressible cakes which are characterized by variation of porosity with respect to distance. The structure is less consolidated at the cake surface and becomes more compact as the plaster is approached. The cake structures as reflected by the porosity variation is intimately tied to particle size, shape, degree of aggregation, and slurry concentration.

A partially coagulated slip, which produces a relatively high cast porosity, will increase J and lower R_c and speed casting. This is acceptable for porcelain products which are densified by the large amount of glassy phase produced during sintering. When producing dense sintered crystalline ceramics, a dense cast from a well-deflocculated slurry is commonly required and J/R_c and the casting rate are lower. The effect of parameter adjustments on the casting kinetics are shown in Figure 3.5. For purposes of quantitative comparison, the time-independent casting rate is conveniently expressed as L^2/t. From the form of the curves in Figure 3.5, it is apparent that product items with thin walls are manufactured more productively. Casting times may be reduced significantly by applying an external pressure on the slurry. Pressure casting is discussed in Section 3.2.
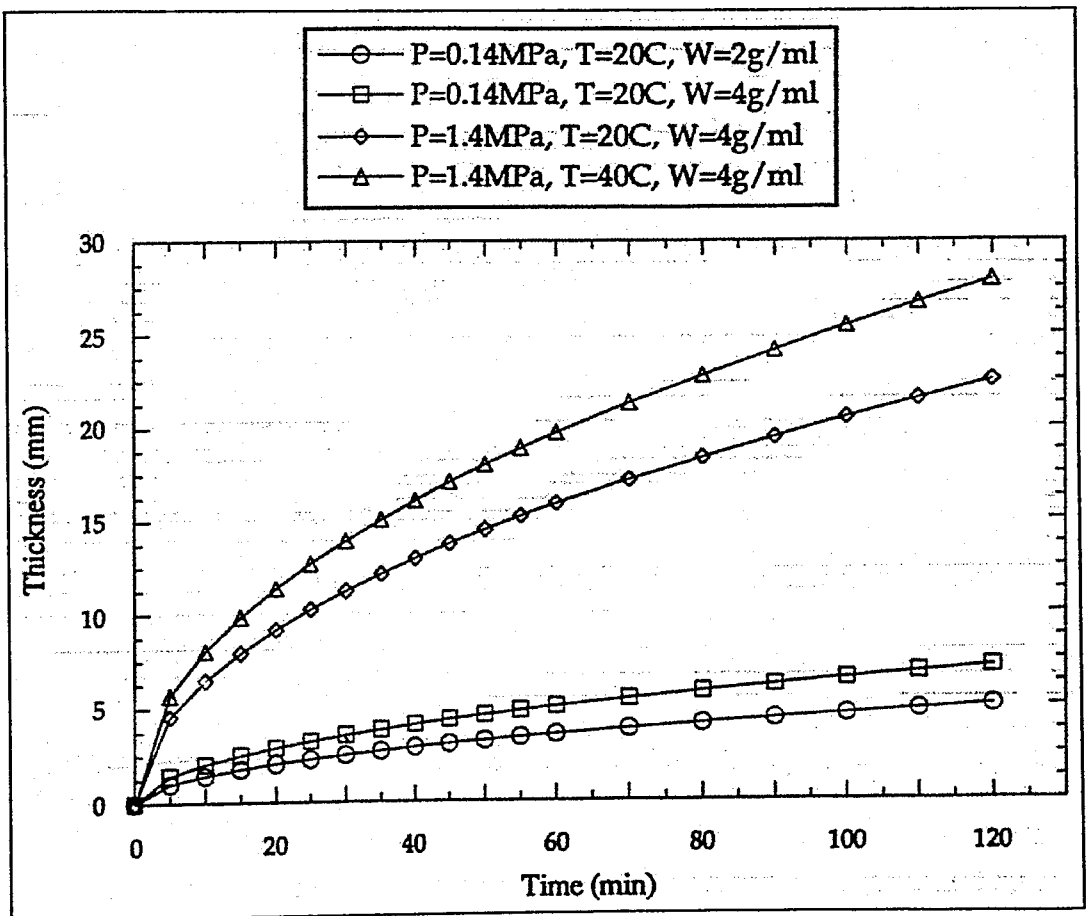
Figure 3.5. Effect of combinations of pressure, solids in slurry, and temperature on thickness of cast with time (calculated for slurry alumina powder deflocculated with polyacrylate deflocculant) [8]

3.1.3. Plaster (Gypsum) Mold

In slip casting plaster (gypsum) molds are used conventionally. Gypsum is a naturally occurring mineral. Chemically, it is calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). Understanding of the role of gypsum molds is important. With the exception of pressure casting, which uses a porous filter, the white ware industries that use casting as a forming method are dominated with plaster molds.

Four important factors affecting the performance of plaster molds include the plaster itself, the chemistry of the water used to make mold, the ratio of the water to plaster, and the mixing technique.

Processing of plaster molds begins with mixing a plaster-water slurry and pouring it into a case mold having the same shape as the final greenware product. After filling the case mold the slurry sets into a rigid shape via the chemical hydration of plaster to gypsum. This process entails the nucleation and growth of needle-shaped gypsum crystals which entangle and become tightly interlocked with random orientation [9]. The pore spaces among these crystals interconnect in all directions to produce irregularly shaped continuous capillaries that are filled with excess water. The freshly set mold is separated from the case mold and the excess water is subsequently evaporated.

During the manufacture of plaster molds, water/plaster ratio is one of the more important criteria because it influences porosity, absorption, and strength [12]. Density (porosity) of a mold can contribute to blocking, due to abnormally fast rate of absorbtion. Other problems associated with porosity are weak mushy casts, surface imperfections, and shrinkage.

Uniformity of plaster feed rates, water/plaster ratio, and weights are extremely critical to minimize mold inconsistencies and maximize absorption rate. This property is also affected by the condition of the mold after drying. A mold that has been calcined will be difficult to use. Controlled drying of plaster molds should minimize calcining tendencies [12]. Ideally, molds are dried at a constant weight and then conditioned

by rewetting, or soaking for a few seconds. This procedure initiates capillary action and evens out the suction of the mold. Thomas [13] summarizes various studies for understanding the effect of water in plaster mold properties with different parameters.

Short service life of plaster molds is a big disadvantage. During the lifetime of the plaster mold a point is reached at which the casting behavior of the clay slip becomes inconsistent, resulting in the removal of the mold from the process. Schulz and Carty [14] studied the effect of ions present in solution which accelerates the dissolution of gypsum, resulting in the change in the casting behavior. They found out that the degradation of gypsum was depended on the presence of ions in the solution, the concentration of the salt solution, and the valence charge of the ions present in the salt solution. They concluded that to increase the life of plaster molds, the ionic strength of the water entering the mold, concentration of magnesium ions and unadsorbed polyacrylic acid present in water needs to be reduced so as to decrease the dissolution rate of the plaster.

3.2. Pressure Slip Casting

The parameter that directly impacts the slip casting rate is the pressure ΔP motivating liquid migration, as indicated by Equation (3.11). The capillary suction of a gypsum casting mold is less than about 0.2 MPa, and for a used mold is commonly less than 0.15 MPa. An external pressure or suction can increase the driving force and reduce the casting time.

Pressure casting has been investigated as a forming technique for porcelain and complex refractory shapes, and mechanized, relatively automatic systems are now used in some industries. In pressure casting, the mold serves as a shaped filtration support, and the casting time is controlled by the slip pressure. The casting time for a particular thickness can be reduced significantly.

Pressure slip casting (PSC) technology is well established in the table and sanitary ware industries but its use in technical ceramic fabrication has been limited.

3.2.1. Slip Chemistry and Rheology

Ceramic particles generally contain atoms that are easily polarizable, thus creating a strong interparticle attraction. Agglomerates defeat the purpose of reducing the scale of mixing. They also can produce spatial variations of packing density that lead to cracking and impaired mechanical properties. A preferred approach for eliminating agglomerates is to establish interparticle repulsion forces by mixing powders in a liquid with dissolved ions or polymers, which then adsorb to the particle surfaces. The former technique (electrostatic stabilization) is most commonly used in slip casting and entails spontaneous formation of a diffuse double layer of dissolved ions surrounding each particle due to the presence of oppositely charged surface sites. The latter method involves adding either neutral (steric stabilization) or charged (electrosteric stabilization) polymers to a suspension. A broad range of rheological properties and slip cast microstructures can be produced from a given powder using the above stabilization techniques [9].

In general, interparticle repulsion results in dispersed slurries that exhibit Newtonian rheology (viscosity is independent of shear rate) at low particle concentrations. At high solids concentrations, the slurries become dilatant (viscosity increases with shear rate) because the apparent volume must increase upon shearing to allow closely spaced particles to slip past one another.

In US Patent 5,593,930, Sato [15] proposed a method for shortening the casting time in pressure slip casting. It was shown that even if only the casting pressure was increased, the casting time would not be adequately shortened. A composition with the necessary chemical and rheological adjustments was given for the slip used in pressure slip casting.

3.2.2. Pressure Slip Casting Mechanics

Fennelly and Reed [16] studied the quantitative mechanics of pressure slip casting an aqueous Al_2O_3 slip deflocculated with an organic polyelectrolyte. The slip pressures

were varying from 0.3 to 3 MPa. They found out that the specific resistance, casting rate and microstructural characteristics of the cakes formed were especially sensitive to the electrophetic mobility of the slip. Fennelly and Reed [16] used a fundamental interpretation of the mechanics of slip casting which lies in an adaptation of pressure filtration theory. The theory includes both the consolidated cake resistance and the resistance of the filter medium as a parameter. The Carman-Kozeny equation describing the laminar flow rate of a viscous liquid through a permeable bed was given as follows [16]:

$$\frac{1}{A}\frac{dV}{dt} = \frac{-\Delta P \varepsilon^3}{k_0 k_t L \mu S_v^2 (1-\varepsilon)^2}$$

(3.3)

where μ is the viscosity of the liquid, $\left(\frac{1}{A}\right)\left(\frac{dV}{dt}\right)$ the volume flow rate/unit area, $-\Delta P$ the pressure drop across the bed, ε the pore fraction, L the thickness of the cake, and S_v the specific surface of the internal capillaries of the bed; k_0 and k_t are the shape-factor and tortuosity constants, respectively. To interpret pressure casting, Equation (3.3) was modified to account for the resistance of the filter medium and to express the variables of the process. The cake thickness, L, is related to the volume of filtrate, V, eliminated according to the following materials balance [16]:

$$LA(1-\varepsilon)\rho_s = w(V + \varepsilon L A)$$

(3.4)

where ρ_s is the density of the solids and w is the weight of solids in suspension/unit volume of liquid in suspension. Equation (3.4) was rearranged and expressed in the form [16]:

$$L = \frac{wV}{A(\rho_s - \varepsilon\rho_s - w\varepsilon)} = JV$$

(3.5)

where J is a contraction for $w/A(\rho_s - \varepsilon\rho_s - w\varepsilon)$. Substitution of Equation (3.5) into Equation (3.3) gave [8]:

$$\frac{1}{A}\frac{dV}{dt} = \frac{-\Delta P}{\mu J V \alpha}$$

(3.6)

where α, the specific cake resistance, is given as:

$$\alpha = k_0 k_t \frac{(1-\varepsilon)^2 S_v^2}{\varepsilon^3} \qquad (3.7)$$

Equation (3.6) is of the general form rate=driving force/resistance. In the equations above, $-\Delta P$ is the hydraulic pressure difference across the cake, but in pressure casting the total pressure difference across the cake and mold was noted. Since the cake and mold are in series, the total resistance, R_T is the arithmetic sum of the individual resistances:

$$R_T = R_c + R_m \qquad (3.8)$$

Equation (3.6) was then expressed in the form:

$$\frac{1}{A}\frac{dV}{dt} = \frac{-\Delta P}{\mu(JV\alpha + R_m)} \qquad (3.9)$$

Rearrangement of Equation (3.9) in the form [16]:

$$\frac{dt}{dV} = \frac{\mu JV\alpha}{A(-\Delta P_T)}V + \frac{\mu R_m}{(-\Delta P_T)A} \qquad (3.10)$$

which provided a working equation for interpreting quantitatively slip casting conducted at constant pressure[16].

A working equation for uniaxial casting, which expresses the cake thickness as a function of the parameters of the casting process was derived for cases where $J\alpha$ is approximately constant. Substitution of Equation (3.5) into Equation (3.9) and inte-

gration gave [16]:

$$L = \sqrt{\frac{-2\Delta P_T A J t}{\mu \alpha} + \left(\frac{R_m}{\alpha}\right)^2} - \frac{R_m}{\alpha} \qquad (3.11)$$

which is a working equation expressing the functional role of the casting parameters. An experimental pressure casting assembly was designed for operation at pressures less than 10 MPa (Figure 3.6) and different slip compositions were pressure cast.
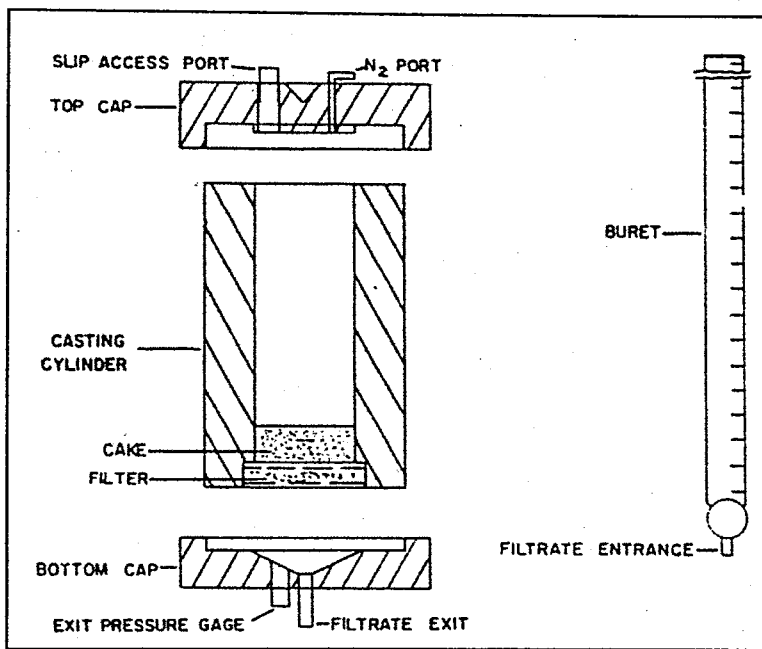
Figure 3.6. Pressure casting apparatus [16]

In another work by Fennelly and Reed [17] compression permeability of Al_2O_3 cakes were calculated using a pressure slip casting system and a pressure of 3 MPa. The compressibility decreased with increasing pressure. Improved deflocculation of slips from which cakes were formed drastically reduced the level and pressure dependence of compressibility.

The compression permeability measurements were made by the apparatus, composed basically of two hollow brass pistons in a stainless steel compression chamber illustrated in Figure 3.7.
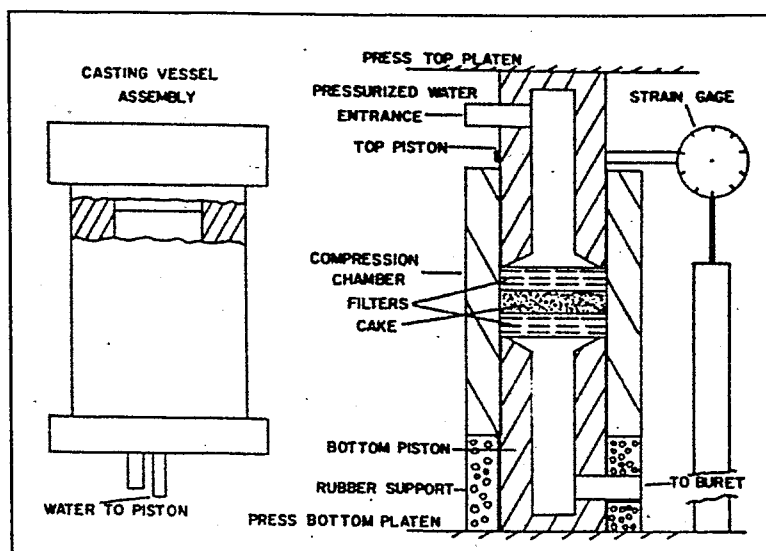
Figure 3.7. Compression-permeability apparatus [17]

Lange and Miller [18] also investigated the effect of pressure on consolidation kinetics of slurries. They pointed out that permeability of bodies consolidated from flocced slurries were very pressure sensitive whereas the well dispersed slurry was pressure insensitive. The applied pressure was in range of 0.04 to 80 MPa.

The particle arrangement in consolidation of the slurry on the molds surface was influenced by the applied pressure. Generally, particle packing density increased with pressure hence permeability of the consolidated slurry decreased. Fennelly and Reed [16] studied the pressure filtration of an aqueous slurry in which the repulsive interparticle forces were systematically increased with additions of a polyelectrolyte. They showed that the packing density of the consolidated layer, and thus its permeability, was strongly dependent on the polyelectrolyte concentration. Concentrations that produced greater interparticle repulsive forces produced the highest packing density.

The pressure filtration device Lange and Miller designed is shown schematically in Figure 3.8. This apparatus was used to obtain data on consolidation kinetics and, upon load removal, strain relaxation. The device consisted of a moving plunger sealed from the outer cylinder with an O-ring. The filter was a partially sintered stainless-steel disk, 0.318 cm thick, backed with a solid steel disk containing several holes. A single sheet of filter paper, which sealed the outer rim of the cylinder and the metal

filter, was used to initiate the consolidated layer buildup [18].
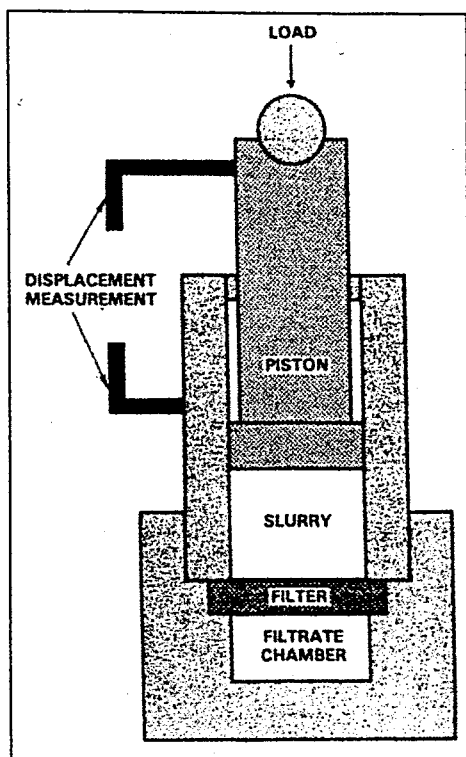
Figure 3.8. Schematic diagram of the pressure-filtration device [18]

Figure 3.9 shows that the consolidated layer permeability, k, is strongly pressure-dependent for the flocced slurries and pressure-insensitive for the dispersed slurries [18].

Lange and Miller applied a predetermined load rapidly to the plunger with the moving crosshead of a mechanical testing machine. To maintain a constant load, the testing machine was used in its load cycle mode, in which the crosshead would stop after the desired load was reached. It would then reactivate when that load relaxed by 1 per cent. The load cycle period increased as consolidation proceeded. The displacement between the moving plunger and the outer cylinder during consolidation was measured with a calibrated, clip-on extensometer. Both load and displacement were recorded during consolidation. The consolidation experiment was terminated when the load cycle period exceeded 1 minute, corresponding to a displacement rate near zero. Pressure exerted on the slurry was calculated by dividing the applied load by the cross-sectional area of the plunger. After consolidation, the specimen was ejected, weighed,

and dried. Assuming that the consolidated body contained only solids and fluid, its solids volume fraction could be measured by weighing the consolidated body before and after drying. The bulk density of the dried body was determined by dimension and weight measurements.

Figure 3.9. Consolidated body permeability as a function of applied pressure for flocced and dispersed Al_2O_3 slurries [18]

Lange and Miller applied a predetermined load rapidly to the plunger with the moving crosshead of a mechanical testing machine. To maintain a constant load, the testing machine was used in its load cycle mode, in which the crosshead would stop after the desired load was reached. It would then reactivate when that load relaxed by 1 per cent. The load cycle period increased as consolidation proceeded. The displacement between the moving plunger and the outer cylinder during consolidation was measured with a calibrated, clip-on extensometer. Both load and displacement were recorded during consolidation. The consolidation experiment was terminated when the load cycle period exceeded 1 minute, corresponding to a displacement rate near zero. Pressure exerted on the slurry was calculated by dividing the applied load by the cross-sectional area of the plunger. After consolidation, the specimen was ejected, weighed,

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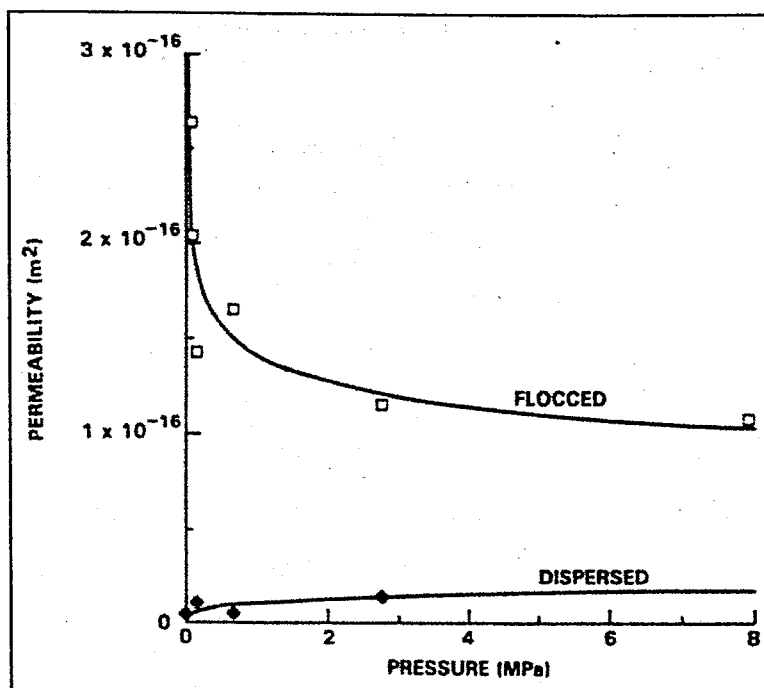
Lange and Miller assumed that the volume displaced by the moving plunger was equal to the volume of fluid forced through the filter, Darcy's Law was integrated to obtain:

$$d = \left[2\frac{k}{\mu} \left(\frac{v_l}{v_0} - 1 \right) P_a t \right]^{\frac{1}{2}} \tag{3.12}$$

where d is the plunger displacement, t the filtration time, P_a the pressure applied to slurry, k the permeability of consolidated layer, μ the viscosity of fluid, v_l, the volume fraction of solids in consolidated layer, and v_0 the volume fraction of solids in slurry. Equation (3.12) shows that pressure filtration should exhibit parabolic rate kinetics. A plot of d versus $t^{1/2}$ should result in a straight line with a slope equal to:

$$\left[\frac{2k}{\mu \left(\frac{v_l}{v_0} - 1 \right)} P_a \right]^{\frac{1}{2}} \tag{3.13}$$

The consolidated layer permeability can be obtained by measuring v_l, after termination of the test if the controllable experimental parameters are known. Figure 3.10 illustrates the work by Lange and Miller in which a linear relation is obtained when the volume fraction of solids in bodies consolidated from the flocced Al_2O_3 slurries is plotted as a function of the log of the applied pressure [18].

Different ceramic compositions can be pressure cast to obtain the desired dense products. Greil et al. [19] studied the pressure filtration of silicon nitride suspensions with constant filtration rate. Pressures up to 10 MPa were used. Using a constant filtration rate instead of constant pressure, a constant growth rate of the cake was induced which provided homogeneous particle incorporation into the growing cake
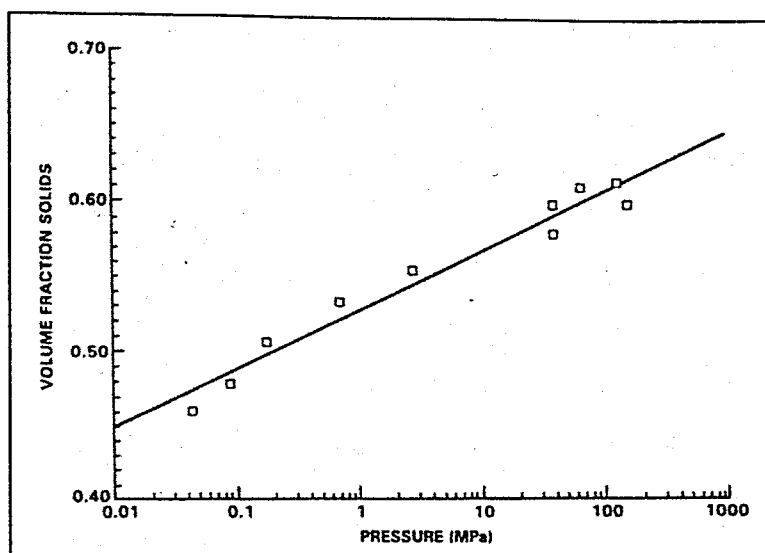
Figure 3.10. The pressure dependence of the solids concentration of bodies consolidated from 20 vol% Al_2O_3 slurries [18]

surface. Darcy equation is again the basic relation used and the effective pressure difference used is interpreted as $\Delta P = \Delta P(\text{suct}) + \Delta P(\text{appl})$. $\Delta P(\text{suct})$ is the suction pressure of the porous mold and $\Delta P(\text{appl})$ is the external pressure on the slip. For pressureless slip casting into the plaster molds $\Delta P(\text{suct}) \approx 0.1$-$0.2$ MPa [19]. Although the suction pressure of the mold also acts in pressure filtration, the applied pressure on the slip is usually orders of magnitude higher, so that the filtration kinetics are mainly determined by $\Delta P(\text{appl}) \approx 1$–$10$ MPa.

The permeability, k, of the consolidated layer was shown to depend on the size, number and shape of the percolation channels in the cast, which are related to particle size and arrangement [19].

Referring to Equation (3.11) Blanchard [2] demonstrated the effect of pressure increase to slip formation. The body thickness at any given casting time was directly related to the slip pressure. As the slip pressure increased, however, the hydraulic pressure on the mold also increased. The materials of construction and the tolerances of fit became increasingly critical and more expensive to achieve as the slip pressure increased.

This leaded Blanchard to the conclusion that different manufacturing systems were required for different applications. When medium pressures 0.3-0.4 MPa were used on large, high production pieces, such as sanitaryware, improved productivity could be achieved at lower capital cost. Rapid improvement in casting time could be achieved as the slip pressure increased from 0.25 to 4 bar (Figure 3.11). The time required to build up a body thickness of 8.5 mm was reduced from 80 to 21 minutes. Increasing the pressure above 4 bar would, obviously, continue to shorten the setup time, but at a continually decreasing rate and at a continually escalating cost in terms of mold material and equipment requirements.
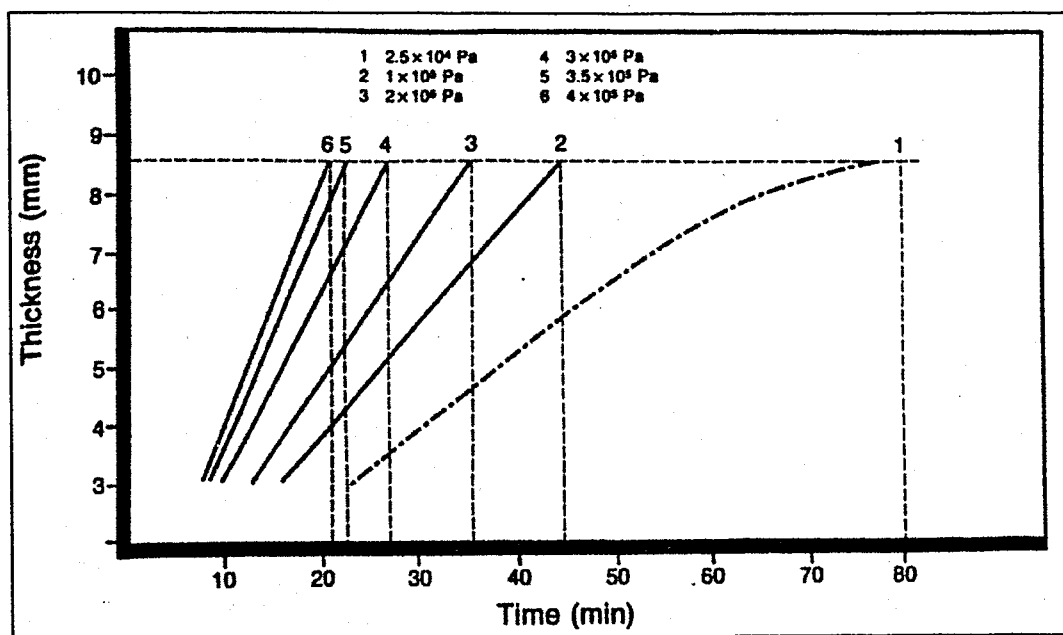
Figure 3.11. The thickness formation is compared between traditional battery casting and casting with overpressure application [2]

The theories used in the works above, all contributes to the following facts as suggested by Leach [20].

- Pressure casting is a filter pressing process, so filter pressing knowledge is applicable.
- Because fewer fines should improve the casting rate, control of the quantity of fines is important.

- The type of deflocculant may be important.
- The quantity of flocculants and deflocculants can affect performance.
- Higher viscosity slip increases casting rate.
- The quantities of organics should be controlled because high organics can clog molds, while low quantities of organics materials can result in weakened cast ware.

4. PRESSURE SLIP CASTING MOLD PRODUCTION

4.1. Need For A New Mold Material

Porous molds are manufactured to serve the ceramic industry in slip casting process. Chapter 3 elaborates this process. While plaster works well as a mold material, it has the unfortunate properties of gradually dissolving when in contact with water and calcining (losing water of hydration) at temperatures above 40°C. For the production of sanitary ware and tableware items, these properties can lead to short mold lives and frequent mold changes as the surface deteriorates and the cast piece begins to change dimension. Plaster is best described as a stiff/brittle material, having a relatively low flexural strength but a high flexural modulus. It clearly has an open cell structure, with a degree of permeability and a mean pore size of 1 to 3 μm. Plaster is used conventionally as slip casting mold. Wallis [21] lists the advantages and disadvantages of plaster molds (Table 4.1).

A new mold material could benefit the manufacturing process. But the information relevant to the development of a new material that would be suitable for replacing plaster is still studied. This study is not simple as the material considerations are important and the process variables are also significant.

Developing a new material first involves the evaluation of its properties, both from a scientific and a commercial viewpoint. The scientific evaluation has to differentiate between those properties that are essential and those that are merely desirable, and this analysis has to be performed for each type of material and process being considered. Typical properties that require evaluation include strength, modulus, permeability, porosity, absorbtion and capillarity. Each process has different requirements that the material scientist has to consider to tailor a material with suitable properties.

Kishima [3, 22], compares various methods for producing a porous material having open pores for use as a filtering medium or casting mold. These are sintering of

Table 4.1. Advantages and disadvantages of plaster molds [21]

Advantages:	Plaster molds are readily available
	For small production runs, the mold costs are lower
Disadvantages:	High weight
	Low strength
	Short service life (80-100 casts maximum)
	Low chemical resistance
	Special preparation of mold is required before casting
	High degree of wear due to mechanical and chemical erosion
	Dimensional accuracy is lost after a few casts
	Poor article quality due to rough surfaces and pinholes
	Uncontrolled water content in the mold
	High consumption of energy for mold drying
	Much space required for mold production and storage
	Much space required for the casting department
	Problematic disposal of old plaster molds
	Difficulties transporting large number of molds
	Low flexibility
	More people required at lower productivity
	Adverse working conditions (humid, hot) in the casting hall
	Highly qualified staff required for operation
	A lot finishing work of cast articles required
Result:	High cost
	Large space requirement
	High fault frequency
	Low yield and quality

metal powder, sintering of powdered thermoplastic resin, sintering of inorganic pow-
der, hydration setting of cement or the like, pressing or stamping of a mixture of a
thermosetting resin and a filler, hardening of a resin liquid containing pore-forming
agent followed by the removal of the pore-forming agent by dissolving, extraction or
evaporation, use of a foaming agent, and polymerization of hardening of a water in oil
(w/o) emulsion, a polyester resin followed by evaporation of water from the hardened
mass.

These known methods of producing porous material having open pores, encoun-
tered one or more of the following problems in connection with the manufacturing
process [3]. First of all, it is to be pointed out that some of these known methods
impractically limit or restrict the shape and size of the product. In addition, some
of these methods often require a heat treatment at high temperature, as well as press
work at high pressure. The method which makes use of the pore-forming agent require
a step of heating or vacuum operation for the removal of the pore-forming agent by
evaporation. Furthermore, these known methods have disadvantages in that it is diffi-
cult to control the pore size or pore diameter. The production steps involved in some
of these methods are generally complicated and difficult to conduct.

Among the aforementioned problems, the control of the pore size or pore diameter
is a particularly important problem [3, 22]. When the porous material having open
pores is used as a material for a filtering medium or casting mold, the principal function
is to separate the particles contained in a fluid flowing therethrough into a first group
which passes through the pores of the porous material and a second group which
does not pass through the pores of the porous material. This function is determined
principally by the diameter of the pores of the porous material. By the use of the
aforementioned known methods, it is quite difficult to control the pore size for the
following reasons [3, 22]:

- In the production of a porous material from metal powder by sintering, it is
  difficult to obtain a pore size smaller than 5 μm because of a specific relation
  existing between the particle size of the metal powder and the surface energy

during the sintering step. Consequently, it is quite difficult to effect control of the pore size to obtain pores on the order of 1 μm.

- In the resin powder sintering method or the inorganic powder sintering method, it is difficult to control the packing density at the molding step although the particle size of the used resin powder or inorganic powder may be controlled. In addition, these known methods suffer from a large change in the pore structure at the sintering step, leading to the result that the pore size is distributed over a wide range to hinder the control of the pore size.

- In the method of mixing a filler with a thermosetting resin followed by pressing or stamping of the mixed material, it is difficult to control the pore size uniformly throughout a product having complicated shape due to uneven molding pressure applied on the different parts of the molded mass or uneven packing of the mixed material, or due to uneven distribution of the thermosetting resin in the mixed material.

- In the case of the hydration hardening of a cement or gypsum, a difficulty is involved in the control of the nucleation and growth of the crystals of the hydrate, and precise control of the mean pore size to obtain pores having an average pore diameter on the order of 0.2 to 10 μm cannot easily be effected.

- The method in which the pore-forming agent is evaporated and removed from the hardened resin containing the pore-forming agent has been proposed for the production of a thin film having pores having an average pore diameter ranging from 0.01 to 0.1 μm. This method cannot be applied to the production of a product having considerably large size and thickness.

- In the method in which a resin in the form of an emulsion type is hardened followed by the evaporation or extraction of the dispersoid, it is not easy to control the size of the dispersoid, and many disconnected or closed pores are inevitably formed. The control of the pore sizes on the order of 0.2 to 10 μm as a mean is also difficult in this method.

Will [4, 23–25] also discusses known methods for producing molds made of porous solid materials to produce die casting, turning and press molding molds. For example water-soluble salts are admixed with hardenable resin molding compositions and after

hardening of the composition, the salts are dissolved out again; or plasticizable plastics, such as polymethylmethacrylate or polyethylene, are pressed into a fine-grained form under the influence of heat, similarly to how porous cast metal parts are produced by sintering fine-grained powder. In other methods, the porosity is attained by pressing inorganic, fine-grained powders, such as quartz, with a small amount of resin added as a binder. Finally, the use of molding compositions made from porous calcium silicate hydrate, which is mixed with coarse-grained plastic and hardened in autoclaves. According to Will these methods have the disadvantage that it is expensive and complicated to make the molds.

According Jung [26] it is not possible to use sintered metals and inorganic materials for producing molds in the ceramic industry, because neither the necessary uniform pore structure, nor the desired surface properties and the simple processing can be achieved. Simple processing is customary in the production of plaster molds. Because of the very fine particle size of clays, the pore size and the pore structure of the mold material are decisive in preventing migration of the clay particles into the pores of the mold whereby the pore diameter would be diminished and the mold would be plugged. There exists a marked difference in performance between mold materials which are broadly porous and mold materials with a defined pore structure and permeability.

Knowing these difficulties and constraints various inventors proposed different methods for producing molds which can be used in both slip casting and pressure slip casting process.

4.2. Manufacturing Of Porous Molds

4.2.1. Plastic Mold

The development of the pressure slip casting process began in the 1980's. The aim was to replace short-life plaster molds with long-life porous plastic molds. According to Seitz [27] plastic molds can be used over 30,000 times with porcelain bodies in tableware industry. The most difficult or problematic bodies for pressure casting in the sanitary

ware industries are those made of fireclay; here, the number of casts normally achieved are around 15,000.

The key requirements for a mold material for use in the pressure casting process are high strength, consistent permeability and low shrinkage. Casting pressures can vary from 0.5 MPa for medium pressure sanitary ware to 4 MPa for pressure casting in tableware [28]. Pressure is the driving force in this casting process therefore, a material with natural capillarity is not required.

Two different manufacturing methods of resin molds are proposed by various authors. The difference is due to the ingredients and process of the material preparation.

4.2.2. Acrylic and Polyester Resin Based Molds

Jung [26] proposed a process for producing casting molds suitable for use in the ceramic industry. The process consists of a polymerized material having minute, open pores and possessing a high degree of mechanical strength and an excellent water permeability. He prepared a castable mixture comprising:

- a major amount of a polymer powder composed of spherical particles and having a polymerization catalyst uniformly distributed over the entire surface of the particles,
- an emulsion of at most about 20 per cent by weight of water, which is based on at least one water-insoluble, liquid monomeric or only partially polymerized compound which is polymerizable to form a rigid polymer and capable of being slightly imbibed the polymer powder. The liquid monomer is the oil phase; and a surface active agent is used for maintaining the emulsion,
- an accelerator for the polymerization of said polymerizable compound.

According to the invention, it is surprisingly possible to produce a porous plastic material having a high density and a uniform open pore structure by casting a castable mixture of a major amount of spherical polymer particles exhibiting a defined grading

and a polymerizable binder, whereby the individual spherical polymer particles are adhered to each other at their contact surfaces by the polymerized binder.

A major amount of polymer means more than 50 per cent by weight, based on the castable mixture. Since the water content is at most about 20 per cent by weight of the mixture; all the other constituents of the castable mixture must be at least about 80 per cent by weight.

Numerous experiments have unexpectedly shown that it is possible to use emulsions containing not more than about 20 per cent by weight of water, based on the mixture of polymer powder and emulsion, as the polymerizable binder, provided that the polymer powder has a polymerization catalyst uniformly distributed over the entire surface of the particles. If the catalyst is dissolved in a solvent and/or added to the emulsion, or if it is suspended in the emulsion, then it is necessary to use more water so that the desired result is not achieved.

Polymer powders are defined as polymeric materials having an average particle size of less than 500 μm. It is advantageous for 80 per cent by weight of the polymer to have an average particle size of less than 200 μm. More preferably, 50 per cent by weight of the polymer powder have an average particle size of less than 100 μm.

Polymer powders composed of spherical particles may be obtained by suspension polymerization. Polymer powder must be capable of slightly imbibing the polymerizable compound or compounds.

As catalysts, lauroyl peroxide, benzoyl peroxide can be used. The catalysts are usually present in amounts in the order of about 1 per cent by weight, based on the polymer powder.

Jung puts the emphasis on the packing and shape of the polymer particles. The size and the size distribution or grading of the spherical polymer particles are largely decisive to the final pore size and pore structure of the polymerized plastic material

produced. When spheres of equal size are packed together, it is possible to produce a mass with voids. A mass with the minimum proportion of voids will result, if spheres of equal size are arranged in a closest packed hexagonal lattice. The ratio of voids to solid matter can be reduced still further by mixing spheres of different size so that the smaller spheres may fill to a certain extent the interstices between the larger spheres. The mixing of polymer particles of different diameters in various proportions is desirable since the physical characteristics of the final mold material are improved. The properties of the final product are related both to the composition of the castable mixture and to the grading of the polymer components.

According to Jung, the use of emulsions of water and liquid polymerizable compound or compounds has several advantages:

- Due to the presence of water, the viscosity of polymerizable binding agent is lowered, thus facilitating uniform mixing of the castable mixture despite of the high proportion of solids in the mixture and the large specific surface of the solids. If no water were present, uniform mixing would only be possible if a higher proportion of liquid polymerizable compound were used. This would however result in an increased filling-up of the interstices between the spherical polymer particles which would change the porosity properties of the material produced.

- Due to the presence of water, the contraction in volume occurring during the polymerization process may be minimized.

- The water additionally serves as a heat transfer medium during the polymerization process thus dissipating the heat of polymerization.

- Furthermore, the water acts as a solvent for the surface active agents and accelerators.

Any liquid monomeric or only partially polymerized compound or compounds polymerizable to form a rigid polymer and capable of being imbibed by the polymer powders may be used to form the emulsion. For example in combination, a poly(alkyl methacrylate), such as poly(methyl methacrylate), poly(ethyl methacrylate) or poly(butyl acrylate), and methyl methacrylate or an unsaturated polyester which

may be dissolved in styrene can be used. Additional suitable polymerizable compounds are mentioned in U.S. Pat. No. 3,256,219 [29]. Particularly useful compounds are monomeric esters of acrylic acid or methacrylic acid, vinyl acetate, vinylidene chloride, styrene or mixtures.

Surface active agents used are capable of maintaining an oil in water emulsion. For a given combination of polymer powder and oil in water or water in oil emulsion different surface active agent may be chosen. It is preferred to use non-ionic or anionic surface active agents. One particular advantage of non-ionics is the relatively low foam height produced in comparison to anionics. The surface active agents are normally used in amounts of about 1 to about 5 per cent by weight, based on the castable mixture.

It is possible, although not absolutely necessary to employ also an accelerator for the polymerization of the polymerizable compound such as an amine accelerator, for example dimethyl-aniline or N,N dimethyl-p-toluidine. The accelerators are in general employed in amounts in the order of about 0.2 per cent by weight, based on the castable mixture.

The components of the castable mixture may be mixed together in an agitator mixer. According to Jung the method of mixing and the order in which the components of the mixture are added is not critical. The water is conveniently added together with the surface active agents. It is particularly important that the mixture of components is capable of being cast. That is, the liquid and solid components in the mixture should be present in amounts effective to form a castable mixture.

The homogeneous mixture of the components may then be cast into a suitable mold and polymerized at ambient temperature. The resultant porous plastic has a uniform pore structure, a high degree of mechanical strength and an extremely good water permeability. The intimate bond between the particles, even if they are very finely divided, results in good surface properties and ensures a satisfactory resistance against external influences, particularly the loosening of particles by flow action even upon prolonged use. The materials used by Jung are listed in Table 4.2.

Table 4.2. Materials used for plastic mold manufacturing [26]

1.	Poly(methyl methacrylate) powder (<300 μm)
2.	Polymerization catalyst
3.	Monomeric methyl methacrylate
4.	Water
5.	Surface active agent
6.	Accelerator

The components listed in Table 4.2 were mixed together, after a stable water-in-oil emulsion was obtained, the mixture was poured into a case mold and polymerized at ambient temperature.

Jung made it possible to produce plastics having a very regular pore structure and a density of more than 0.8 gr/cm^3 as well as about 30 per cent by volume of open pores. By a *regular pore structure* is meant that the pores are of approximately the same size and are uniformly distributed throughout the polymerized material. Although the polymeric materials thus obtained are particularly suitable as casting molds for pressure casting of ceramic materials, they are also useful as filters for liquid and gaseous media and other porous shaped articles.

Will [30] in German Patent DE 1,928,026 describes the production of porous molds from water in oil emulsions which in addition to water and monomers contain swellable fine-grain polymer particles. Such a polymerization system consists of polymethlyacrylate (PMA), methylmetacrylate (MMA) and water in the weight ratio of 1:1:1. According to his invention, after adding hardeners and accelerators, the pourable emulsions are cast into a corresponding mold and hardened. When hardening sets in, the emulsion becomes unstable because of the removal of the monomer and the swelling of the polymer part. The phases show coalescence, and relatively coarse pores form having a diameter of 10-40 μm. This means that a high pressure of about 15–40 MPa is necessary for ceramic body formation using such mold materials. Mold materials produced by this process are therefore suitable for pressure casting. The cost of mold production and additional machining is high because of the acting pres-

sure during use and the special polymer beads required for production, so that this conventional method is suitable only for special industrial production of porous mold materials as a substitute plaster of Paris.

In another invention Will [25] describes the production of porous mold materials having the properties typical of plaster of Paris, by which ceramic bodies can be produced from ceramic materials in a short time without the use of pressure. To achieve a suction action effective for the ceramic body formation, the emulsion was prepared in a viscosity within the range of 1600-5000 cP, particularly by adjusting the stirring of mixing conditions and the duration of mixing. The detailed information of this process is described in a German Patent by Will [31]. With these conventional mold materials the ceramic body formation rate was higher the higher emulsion viscosity set during the production of the water-in-oil emulsion. Compared with plaster of Paris, with these mold materials the ceramic body formation rate was increased by adding substances such as calcium sulphate dihydrate, sodium disilicate or disodium tetraborate as regulators for the resultant porosity [25]. Figure 4.1 shows the change in forming rates when a mold is produced according to this proposed method. By applying pressure to such molds the ceramic body formation time could be additionally shortened using a pressure in the range of up to about 0.3 MPa gauge. However, the added pore-width regulator substances had the draw-back of leading to considerable shrinkage, which was extremely unfavorable in the production of castings from ceramic materials, in which particular dimensional accuracy was required throughout.

According to Will [25] the porous plastics mold materials were produced from hardenable water in oil emulsions corresponding to German Patent DE 1,928,026, however no special polymer powder for making the emulsions unstable was used. Although in DE 1,928,026 the produced pressure casting molds were dewatered with compressed air after each casting and the ceramic bodies formed could be released from the mold with compressed air, in US Patent 5,033,950 the produced mold materials could not be treated in the same way. The increased resistance to flow due to the smaller pore width hindered dewatering and ceramic body release using pressure. Instead the ceramic bodies of such mold materials were released by virtue of the shrinkage arising
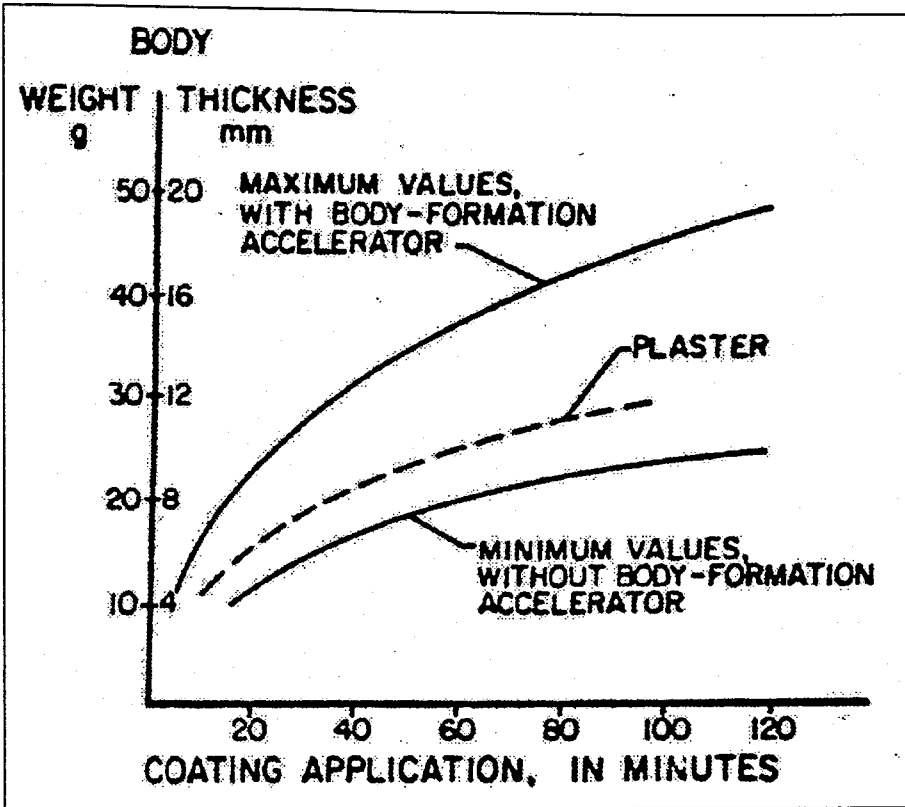
Figure 4.1. The change in forming rates in plastic molds [25]

during dewatering. For this reason the advantages connected with the fine porosity of this material could not be fully utilized technically in the desired manner. The shrinking-out of the ceramic body from the mold required time. What was to be aimed at was an accelerated ceramic body formation under slight pressure, with the release of the ceramic body from the mold with compressed air set to the required time. The mold material of US 5,033,950 behaves in this respect as plaster of Paris, which likewise does not allow release of the casting with compressed air on account of its fine porosity. In this case this is aided by producing additional porosity in the plaster of Paris mold. Compressed air is blown in through a channel system provided in the mold and penetrates by pressure through the mold. This produces a coarse pore system through which the compressed air can escape. In this way a permeability is achieved which makes it possible to release the ceramic body with compressed air.

The object of Will [32] in European Patent 516,224 was to provide plastics-based porous mold materials which could be produced with little or no shrinkage and

which were suitable for both pressureless and pressurized forming of ceramic castings. The porous, open-pore water absorbent mold materials of the invention consist of a hardened, filler containing plastics material and have a water-fillable pore volume of at least 10 per cent of the total volume. They are characterized by containing, as filler, short fibers having a length of 1-6 mm and in a quantity of up to four weight per cent with respect to the weight of the plastics content excluding additives. The basic concept of the invention of Will [32] was that by adding even very small quantities of short fibers a considerable reduction in shrinkage could be achieved, The mold materials contain between 0.5 and 10 weight per cent of short fibers with respect to the weight of the plastics content excluding additives. Will preferred particularly, short fibers of textile materials, carbon and/or glass as fillers, and especially glass staple fibers. In addition to the primary short fibers, which served to reduce shrinkage, the mold materials according to the invention was also containing further fillers, which were of granular, spherical or spheroidal shape as explained in US Patent 5,033,950. Suitable such additional fillers were glass micro-beads, hollow glass micro-beads, hollow ceramic micro-beads and granulated polymers from powder form to fine granular form, in particular those which were only difficultly soluble or only swellable in the polymerization system used for producing the mold materials. These further fillers were contained in a quantity of up to 15 weight per cent with respect to the total dry weight.

The plastics material used by Will consisted of a homopolymer or a copolymer of monomer units deriving from styrene, methylacrylate or ethylacrylate, and methacrylic esters, in particular methylmethacrylate or ethylmethacrylate. Good properties were obtained if the plastics material contained polymer blocks deriving from an unsaturated polyester. The pore size of the mold materials prepared by Will [32] is in the range of 0.1 to 0.5 μm and is adjustable. The mold materials of his invention can be produced by any desired emulsion polymerization process.

Will prepared a water in oil emulsion (w/o) with an oil phase consisting of one or more polymerizable liquid monomers using emulsifiers. The water content corresponded to the desired pore volume. The oil phase was polymerized in the presence of a polymerization initiator in a mold, and if necessary the water was removed from the

mold material obtained after polymerization. This process was characterized by addition of short fibers of a length of 1-6 mm to the polymerization system in a quantity of up to 4 weight per cent, with respect to the weight of the polymerizable part of the emulsion excluding additives.

In accordance with US 5,033,950, for achieving a desired permeability or water suck-off action of the mold material it is advantageous to set the degree of dispersion of the water phase of the w/o emulsion by mixing to achieve a viscosity within the range of 1600-5000 cP, particularly by adjusting the mixing time and the mixing intensity. The further fillers are added to the polymerization system, in particular to the w/o emulsion, preferably in a quantity of up to 35 volume per cent with respect to the polymerization system including the water. According to the invention of Will it is advantageous to use w/o emulsions with an oil phase containing an unsaturated polyester resin, and a liquid prepolymer predominantly of methylmetacrylate in a quantity of 40-70 weight per cent. Calcium sulphate dihydrate, sodium disilicate or disodium tetraborate can be added to the w/o emulsion as permeability regulator. Addition of this regulator unfavorably increases the shrinkage of the mold materials, this shrinkage is restricted by the addition of short fibers according to the invention. Therefore advantageous effects of the permeability regulator can be fully utilized. These regulators are advantageous added in a quantity of between 2 and 12 weight per cent with respect to the weight of the polymerizable part of the emulsion. The polymerizable liquid monomer or monomers are used according to the invention in a quantity of between 30 and 78 weight per cent with respect to the weight of the emulsion.

Powdered polymers swellable in the oil phase of the emulsion, polymethylmetacrylate polymer beads, barite and/or ground quartz can be used as further fillers [32]. The molds used for producing ceramic castings can be formed from the mold materials according to Will's invention either by turning, milling, drilling, or by direct casting in a mold.

According to Will [32] molds of porous plastics can be produced by which considerably quicker ceramic body formation without pressure or under a low pressure of

about 0.5-5 MPa gauge can be achieved (Figure 4.1). This effect is particularly due to the small pore width of about 0.1 to 0.2 μm achievable by this process.

4.2.3. Epoxy Resin Based Mold Manufacturing

Kishima [3] proposed a method of producing porous material having open pores, comprising the steps of preparing a slurry from a mixture comprising a bisphenol-type epoxy resin, a specific mixture amide compound as a hardener, a filler and water. The slurry is cast in a water-impermeable mold and hardened while containing the water and dehydrating the hardened body.

The filler used in the method of the invention is of a material which can be bound by means of a bisphenol-type epoxy resin. The material of the filler should have a small content of soluble salts, or otherwise a large contraction will occur during the hardening. The material should also be one which permits control of the particle size. Preferably, the filler is constituted by an inorganic material having a large surface energy such as powders of silica stone or silica sand.

Kishima have found that the mean pore size in the product porous material is linearly increased while the viscosity of the slurry for the production of porous material having open pores is linearly decreased as the rate of amide compound of the monomeric fatty acid in the hardener is increased. With this knowledge, the inventor have accomplished the present invention through seeking for the optimum conditions such as the kind of the monomeric fatty acid, kind of the ethyleneamine, and the ratio between the fatty acid and ethyleneamine, in relation to the properties or characteristics in the production of the porous material and the properties of the hardened porous material.

In another proposed method Kishima [22] produces a porous material having open pores comprises the steps of preparing an emulsion slurry by vigorously agitating a mixture comprising (i) a glycidyl type epoxy resin, (ii) a first hardener selected from the group consisting of modified polyamine hardeners each being prepared by modifying

a polyamine hardener with a modifier, amine hardeners and mixtures thereof, (iii) a second hardener selected from the group consisting of polyamide hardeners, (iv) a filler and (v) water, casting said slurry in a water-impermeable mold, and hardening said slurry while it contains water. A large size molded product having a complicated contour and having open pores whose average pore diameter ranges from 0.2 to 10 microns can be produced with high dimensional accuracy. In this method Kishima found that the pore size of the hardened product may be controlled within a wide range without causing increase in contraction or shrinkage of the hardened mass by using, in addition to a polyamide hardener, a modified polyamine hardener prepared by modifying a polyamine hardener with a modifier and/or an amine hardener and by changing the mixing ratio between the polyamide hardener (second hardener) and the modified polyamine hardener and/or amine hardener (first hardener).

Later Matsumoto [33] proposed an enhanced process in which a porous material having open pores including, an epoxy compound having at least one epoxy ring in the compound, a hardener capable of reacting with the epoxy compound to harden the epoxy compound, a filler and water. This mixture forms an emulsion slurry having a low viscosity and containing the soluble salts uniformly dispersed. The resulting emulsion slurry is cast in a water impermeable mold and then hardened. While it is maintaining the water content, the soluble salts are added to the mixture. The method makes it possible to produce a large scale porous material having open pores and a complicated shape whose shrinkage factor during hardening and water and air permeabilities are controlled to desired levels respectively while scattering is reduced.

According to Matsumoto one drawback of Kishima's method is; though it permits control of the pore size of the resulting porous material, it cannot provide porous materials having open pores having a relation between the pore size and the air and water permeabilities which is always kept unchanged. More specifically, the water and air permeabilities are sometimes insufficient even if the pore size is satisfactorily large. This uniformity in the relation between the pore size and air and water permeabilities of the porous material having open pores is very important when the porous material is used as filtering mediums, air diffusion mediums and casting molds used in industry.

Also, control of the water and air permeabilities of porous materials is very important in industrial applications, but it has been impossible to control them according to the conventional techniques.

Furthermore, it is necessary to eliminate the scattering in shrinkage of porous material encountered during hardening of the same if high dimensional accuracy is required, but the conventional techniques cannot solve this problem at all.

Matsumoto provided a method of producing a porous material having open pores in which soluble salts are compulsorily added to an emulsion slurry comprising an epoxy compound having at least one epoxy ring in the molecule, a hardener capable of reacting with the epoxy compound to harden the same, a filler and water for controlling the shrinkage of the slurry during hardening and water and air permeabilities of the resulting porous material to desired values respectively while reducing the scattering in the shrinkage as well as the water permeability and the air permeability.

In another method Matsumoto [34] developed his invention and proposed a method to produce a mold for pressure-cast-molding a ceramic article having a filter material made of an open-cell porous material. The open-cell porous material is prepared by stirring a mixture of a resin material, a microballoon, a curing agent and water to provide an emulsion slurry, casting the slurry in a water-impermeable mold and curing the slurry in the water-containing state. The portions occupied by the water during the preparation of the porous material mainly form open pores.

In proposed methods the control of the pore sizes of the open-cell porous materials is done. However, the weights of the porous materials are very important when they are used as industrial materials such as filter mediums, air diffusion materials and mold materials. In particular, if these porous materials are used as mold materials for pressure-cast-molding ceramic articles, most of which have complicated shapes as observed in case of sanitary-wares, the parting of a mold is correspondingly complicated and a large number of split molds and cores must be used. In such case, the resulting molded products are often transferred while a part of the mold is held within the

molded article and/or hangs down from the exterior part during releasing process after completion of the molding. Accordingly, if the weight of the mold is heavy, the molded article is sometimes deformed due to the weight.

The mold is heavy in some cases when the surface layers occupy the space within the mold at a high rate of occupation and the weight is almost determined by the weight of these surface layers. This is observed when the mold has a complicated shape. Matsumoto used microballoons as fillers with low specific gravities, for lightening the open-cell porous material. Microballons are much more lighter than previously used filler materials.

4.2.4. Selection of the Porous Mold

So far proposed methods give a reliable mold which can be used repeatedly in pressure slip casting process. Except Will [25] who suggested molds for use in both pressure and capillary slip casting process. As explained pressure slip casting molds have relatively big pore sizes which helps easy liquid flow. In contrast, the method proposed by Will gives the use of a plastic mold with smaller pore sizes which makes use of capillary action as in gypsum mold.

Matsumoto [35] and Will [25, 32] suggest a method for producing porous plastic mold to replace plaster molds in slip casting. As is the case with the slip casting process using the plaster mold, the cost of the required molding facility is smaller for an arrangement because no external pressure is applied to the slurry. It is an economically better choice to use a water-resistant mold material rather than plaster in order to increase the service life of a mold, and deposit the slurry mainly under capillary attractive forces of the mold material. There are two different goals in porous mold manufacturing:

1. Replacing plaster molds with plastic molds which have the same capillarity.
2. Producing high permeability plastic molds for use with pressure.

A material with high permeability and a relatively large mean pore size would not be readily appropriate for slip casting but it is applicable to pressure slip casting, provided that its strength and modulus are also adequate. Equally, materials with lower permeability and smaller mean pore sizes are unlikely to be suitable for pressure casting applications, but may be applicable to capillary casting (slip casting), again depending upon other properties such as their strength, modulus and casting ability.

There is an attempt to produce a plastic based material to use in *slip casting* that replicates the natural casting ability of plaster, while still enabling ready dewatering between casts. This combination of properties enables the molds to be used continuously without the need for mold drying, which typically limits plaster molds to a maximum of three casts per day. The key objectives for developing the material were:

- tight pore structure,
- inherent affinity for water,
- large surface area.

The combination of these three properties enables the material to replicate the natural capillarity found with plaster, while still enabling rapid dewatering between casts, which gives greatly enhanced productivity.

As explained earlier (Section 3.2), rapid improvement in casting time can be achieved as the slip pressure is increased. The pressure casting contributes to an increase in the productivity because the rate at which the slurry is deposited by the pressure casting is much higher than the plaster slip casting due to direct pressurization of the slurry. However, the direct pressurization of the slurry requires the provision of a strong piping structure, a strong mold structure, and a strong press structure for combining mold members (a molding space in a mold is usually formed by combining a plurality of mold members), resulting in a huge cost required for the molding facility.

5. EXPERIMENTAL STUDY

Theoretical aspects of slip and pressure slip casting have been explained in the previous sections. The heart of these slip casting methods is the mold, which in fact is basically a filter.

Permeability of filter to clean liquid is given by Darcy as shown in Equation (2.4). Particle size, form and porosity is related with the permeability of a porous medium in equation given by Kozeny-Carman:

$$k = \frac{\varepsilon^3}{K\,(1-\varepsilon)^2\,S_v^2} \tag{5.1}$$

There is a great deal of experimental evidence that for non-consolidated porous masses whose pores are non-orientated, the constant K can be taken as 5 within a range of porosity of about 0.9 to 0.30 [36]. The most regular and uniform porous mass is that consisting of spherical shape and of uniform diameter d_s. Specific surface area is $S_v = \frac{6}{d_s}$ for this structure. Hence Equation (5.1) can be written as:

$$k = \frac{\varepsilon^3 d_s^2}{5\,(1-\varepsilon)^2\,36} \tag{5.2}$$

This equation obtained is used for calculating the pore diameters of the particles in the mold for measured permeabilities.

As described earlier the application oriented properties imposes a certain filter selection. Plaster molds are not suitable for pressure casting. A porous mold having a uniform open pore structure is needed. An object of the experiments is to manufacture porous plastic molds with different ingredients contributing to different physical properties. Acrylics and polyester resin based molds will be manufactured. As explained in Section 4.2.2 the plastic material is cast as an aqueous emulsion and then cured.

The emulsion polymerization is a heterogeneous reaction process in which unsaturated monomers or monomer solutions are dispersed in a continuous phase with the aid of an emulsifier system and polymerized with free-radical initiators.

Ingredients for a typical emulsion polymerization system include the continuous phase, normally water; monomer, monomer mixture, or monomer solution; emulsifier and stabilizers; and initiator system.

5.1. Materials Used

The composition of acrylic resin based molds were given in Section 4.2.2. Molds are manufactured according to the recipes given by various authors. A list of materials used in the experiments are given in Table 5.1.

Table 5.1. Materials used in porous plastic mold manufacturing

No:	Material	Description
1.	Resin	Unsaturated polyester of maleic acid and glycols
2.	Monomer I	Styrene
3.	Monomer II	Methacrylic acid methyl ester
4.	Polymer Powder	Fine-grained spherical polymethylmethacrylate.
5.	Catalyst	Benzoyl peroxide
6.	Emulsifier	w/o emulsifier and surface active agent
7.	Accelerator	N-dimethyl-P-toluidine
8.	Filler	Microbeads of glass
9.	Water	Tap water, drink water

5.2. Equipment Used

Throughout the laboratory testing period several apparats were utilized. Permeability tests were done in a pressure slip casting experimental setup. The components are shown in Figure 5.1.
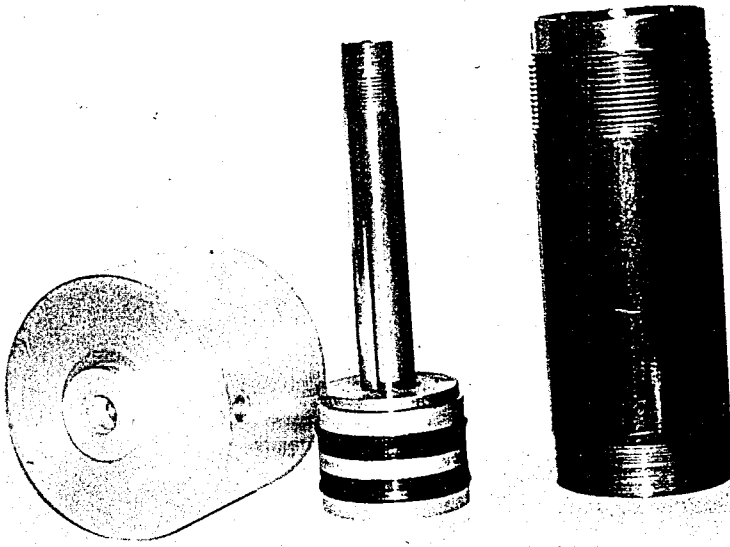
Figure 5.1. Components of the pressure slip casting setup

The steel cylindrical pressure chamber is screwed to the aluminum bottom part which contains the mold. Channels provide the expulsion of water. The slip may be poured into the cylinder and simply pressed with a piston. This setup is adapted to a hydraulic press used by Boz [37], and is shown in Figure 5.2. Top of the pressure chamber can be closed. A cap with pressure regulator can be adapted to the system by which pressure inside the chamber is adjusted using an air compressor. This setup is used in permeability measurements.

PRESSURE SLIP CASTING
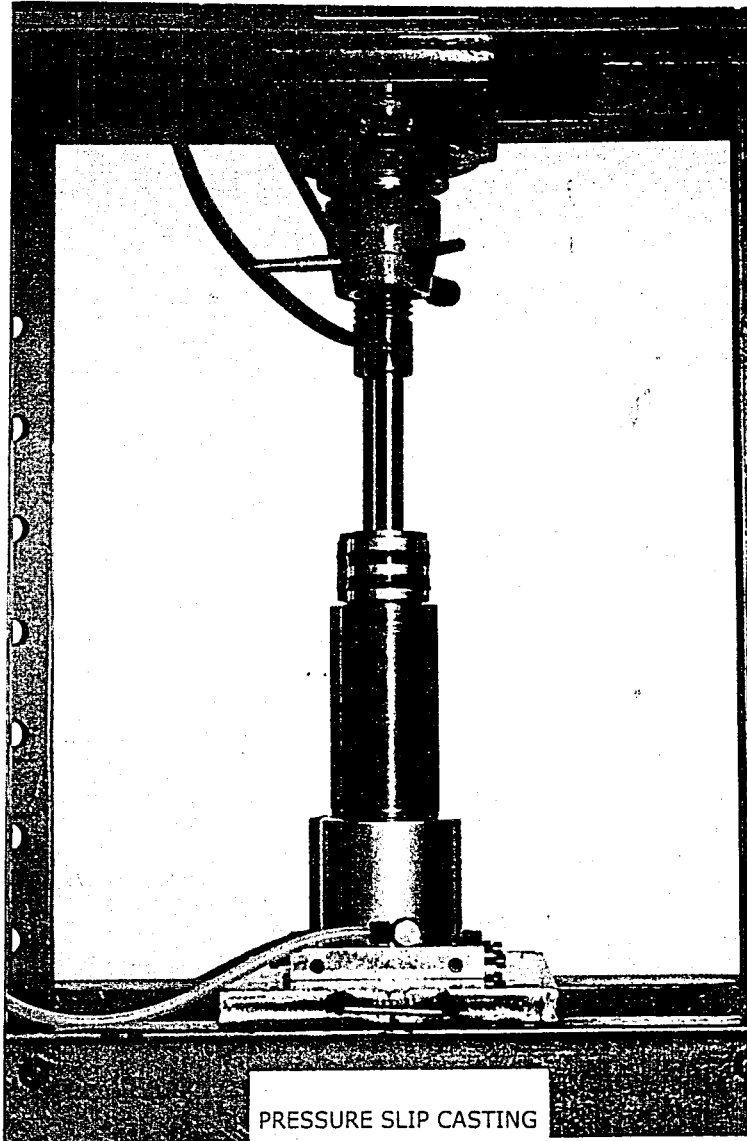
Figure 5.2. Pressure slip casting setup

5.3. Manufacturing of the Porous Plastic Mold

An object of the experiments is to understand the effect of powdered polymer component to pore size and pore size distribution of the final product. Jung [26] suggested to use a mixture of polymer powder with varying particle sizes for good mechanical strength and uniform porosity. The size and the size distribution or grading of the spherical polymer particles were believed to be largely decisive to the final pore size and pore structure. To demonstrate this effect, 5 different compositions were cast. Table 5.2 lists the specimen numbers and the polymer powders used.

Table 5.2. Properties of the specimens cast

Specimen No:	Powder Used	Average particle diameter (μm)
1	Polymethylmethacrylate Powder	40
2	Polymethylmethacrylate Powder	60
3	Polymethylmethacrylate Powder	100
4	1:1 mixture of 1 and 3	70
5	1:1:1 mixture of 1, 2 and 3	70

During polymerization the water component is removed, thus providing in the matrix a system of open cells whose aggregate volume is equivalent to the quantity of liquid water which has been removed. In experiments the water fraction is kept constant. For improving the mechanical properties of the cast, filler is added [25].

Polymerization is a chemical process and materials used are highly sensitive to environmental conditions. The experiments were made at a temperature of 18°C.

Procedure for manufacturing the molds is as follows. The water component is stirred slowly with a mixer (speed 90-120 rpm) which already contains the catalyst and the surface active agent. The polymer powdered is poured into the water and stirred until a complete dispersion of powder in water is achieved. The mixture is than left for

deairing for a couple of minutes. In a separate vessel monomer which already contains the accelerator and w/o emulsifier is stirred with the filler for about a minute. Hollow glass spheres may be used as fillers. Using hollow fillers retards sedimentation and gives a uniform distribution in the monomer phase before final mixing. The water-powder mixture is than poured into the monomer containing vessel and after stirring 60-120 seconds the emulsion is poured into the case molds. Five specimens were cast according to this procedure.

The polymerization process takes place in the mold. The mixture has a general balance among the forces of attraction and repulsion which water and monomer exert upon themselves and each other. This balance tends to prevent coalescing of the emulsified water droplets thus discourages breaking of the emulsion. Polymer powder introduces a condition of imbalance into the system. As the polymer swells or dissolves, it withdraws into itself some of the monomer phase. The portion of the oil phase which thus becomes trapped in swollen polymer particles is no longer able to balance the forces in the water phase to same extend as when the emulsion was first formed. By the time the monomer phase has been withdrawn sufficiently to encourage substantial coalescence of the water droplets, the viscosity of the system increases where only very short range movement of the water droplets is possible. Although the approximate state of distribution in which the water existed in the emulsion is preserved, adjacent water droplets are apparently pushed or drawn closer together and in some cases even caused coalescence. Upon solidification of the mass in the foregoing condition, the resultant product has far more open cells than have been obtained when the polymer powder is omitted [38]. Time of reaction is approximately 2 hours. Complete curing is established in approximately one day. The voids between swollen or dissolved particles of polymer in the finished product contain to a varying extend the residues of the walls of cells formed by polymerization of the monomer, so that where the particles and therefore the voids are relatively large, the quantity of cell residues in the voids is also greater, and the tendency undue enlargement of the pore size is thus counteracted [38]. After two hours the cast mold discs can be easily removed from the polyethylene case molds. The products are shown in Figure 5.3.
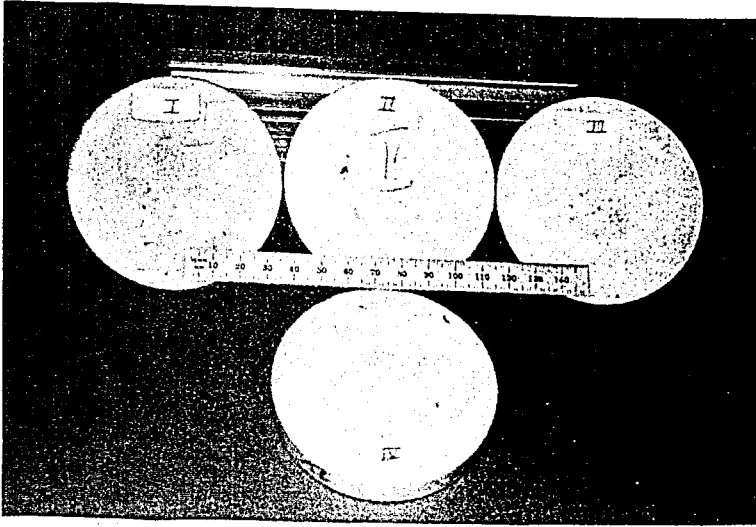
Figure 5.3. Cast specimens

Another mold material, specimen 6 was also cast according to Will [32]. The ingredients in example 7 of Will's work were used to prepare the mixture.

The procedure according to Will is: To the resin dissolved in the monomers, emulsifiers, catalyst or accelerator and powdered polymer are added and mixed in and then the water is added, stirring slowly, and the water in oil emulsion is formed. Depending on the temperature and catalytic action, a solid mold part, which contains water, is obtained after approximately 15 to 120 minutes, the weight of which is reduced after drying by approximately the proportion of emulsion water. The pore volume corresponds approximately to the amount of water incorporated into the emulsion and is predominantly open. Unsaturated polyester resin and monomers were mixed with the glass beads. Water, catalyst and a small amount of powder polymer were mixed in a separate vessel and than poured into the monomer resin mixture. A water in oil emulsion was obtained.

It took approximately 20 minutes for the mixture to have an observable viscosity increase in 18°C. Will suggested a two minutes stirring before casting the mixture. After 20 minutes the emulsion was cast into the case mold and left there to harden under ambient conditions.

For comparison a plaster mold is also manufactured. For 100 gr of plaster 50 gr of water is used to prepare the mixture. Plaster and water are stirred for a couple of minutes and then cast into case mold. Modelling plaster is used as plaster material.

The case molds were prepared for casting the resin (Figure 5.4). They are designed for easy recovery of the porous plastic molds after hardening. The polyethylene case molds have an inner diameter of 80 mm and 50 mm.
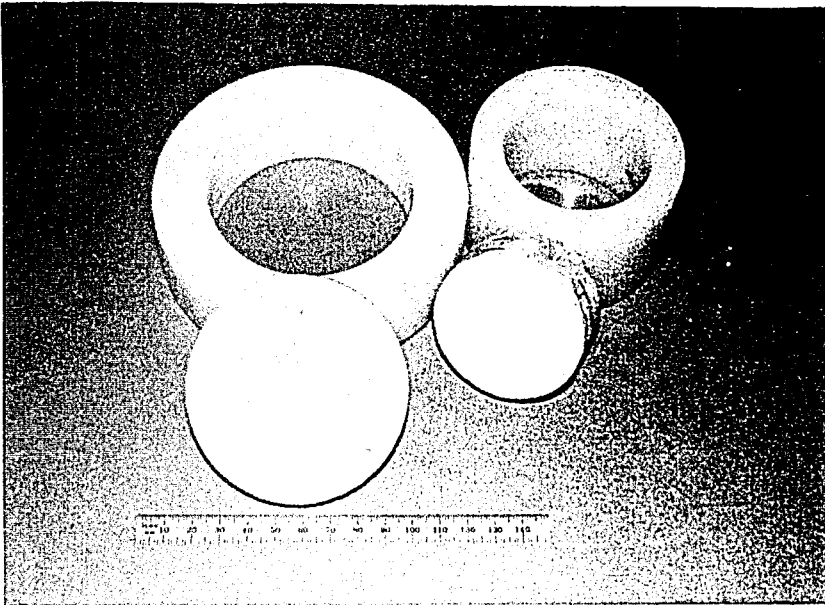

Figure 5.4. Polyethylene case molds used in casting the resin

6. RESULTS AND DISCUSSION

6.1. Pore Volume and Density

Pore volume measurements are made to the cast specimens. After curing water was expelled by pressurized air and evaporation in a furnace. All the specimens were held in furnace for 2 hours at 50°C. The dry weight of the specimens is measured by a digital balance, and the dimensions are measured by caliper. Because the specimens are used as cast, slight variation in dimensions is observed. However geometrical shapes were uniform and suitable for measuring the apparent volumes. The apparent density of the specimens are calculated by simply taking the weight/geometrical volume ratio. After measuring the volumes and weights, distilled water is forced in to the specimens. This is done by placing the specimens in a well sealed pressure chamber (Figure 6.1). A pressure of 0.2 MPa is applied for 20 minutes. The specimens are then weighed. This gives the total weight of the penetrated distilled water. Since distilled water is used pore volume of the specimens can be calculated by:

$$\text{Pore Volume} = \frac{W_{wp}}{\rho_{dw}} \tag{6.1}$$

where W_{wp} is the weight of the water penetrated into the pores and ρ_{dw} is the density of the distilled water.

The water component used in all the specimens was 25 per cent, hence the anticipated pore volume is 25 per cent. However because relatively small amounts of mixtures (max 140 g) are cast deviation occured from theoretical values. Specimen 1 and 2 have good accuracy in pore volume calculations. Polmethylmethacrylate powders used in these two specimens had an average particle diameter of 40 and 60 μm. Specimen 3 had 100 μm sized particles and specimen 4 was a mixture of two different sized polymer particles (40 μm and 100 μm). Specimen 5 was a mixture of three different particle sized polymer powders. The measured pore volumes are listed in Table 6.1.

Table 6.1. Experimentally measured pore volumes

Specimen No.	Pore Volume (%)
1	25
2	24
3	20
4	29
5	33

Another specimen is also cast (specimen 6) according to Will [32] and the obtained pore volume is 24 per cent. Specimen 7 is plaster and the measured pore volume is 46 percent.

In all specimens except plaster the water content used was 25 per cent by weight. The apparent density of the cast specimens are listed in Table 6.2. In the specimens one to five the use of polymer powder results in higher density. In these specimens approximately 30 percent of the mixture is polymer powder. In specimen 6 however, polymer powder used is only four percent of the mixture.

Table 6.2. Apparent density of the molds

Specimen No.	Apparent Density (g/cm^3)
1	0.85
2	0.84
3	0.85
4	0.84
5	0.80
6	0.70

6.2. Permeability

The permeability measurement is made for comparison of the cast specimens. Tests are made in the pressure slip casting setup with the components shown in Figure 5.1. Porous disc mold with a diameter of 8 cm is placed in the bottom of the chamber and a known volume of water is poured inside the cylinder. Top of the pressure chamber is closed. A cap with a pressure regulator is adapted. Compressed air is forced into the sealed pressure chamber (Figure 6.1). A pressure of 0.1 MPa was maintained inside the chamber using the pressure regulator. The Autocad drawing showing the cross section of aluminum bottom part is shown in Figure 6.2. Water is forced out from the chamber through the channels opened.

Time required to expel the water is recorded. Six runs are made for each mold. The data obtained is given in Table 6.3.

Table 6.3. Measured permeability of the specimens

Specimen No.	Permeability k (m^2)
1	2.10×10^{-12}
2	1.73×10^{-12}
3	1.43×10^{-12}
4	2.37×10^{-12}
5	1.67×10^{-12}
6	2.69×10^{-13}
7	5.25×10^{-13}

From the data obtained above an average and approximate particle size of polymer powder in the molds can be calculated. If we assume that the pores are formed in the interstices between the polymer powders which are closed packed and same in size the average particle diameters can be calculated by using Equation (5.2).

After calculating the pore volumes, and permeability of the specimen molds the particle sizes are calculated. The average particle sizes are listed in Table 6.4.

Table 6.4. Calculated particle diameters according to Equation (5.2)

Specimen No.	Particle Size (μm)
1	117
2	114
3	143
4	94
5	61

Darcy's law as stated before relates the volume flux with permeability, the liquid viscosity and the pressure gradient. Force fields such as gravity are neglected as driving force and a uni-directional pressure gradient is presumed. Darcy's law is necessary to obtain the material property permeability which solely depends on the properties of the porous medium (porosity ε, particle diameter d_s). Permeability is affected by the pore volume and particle size hence pore size of the mold.
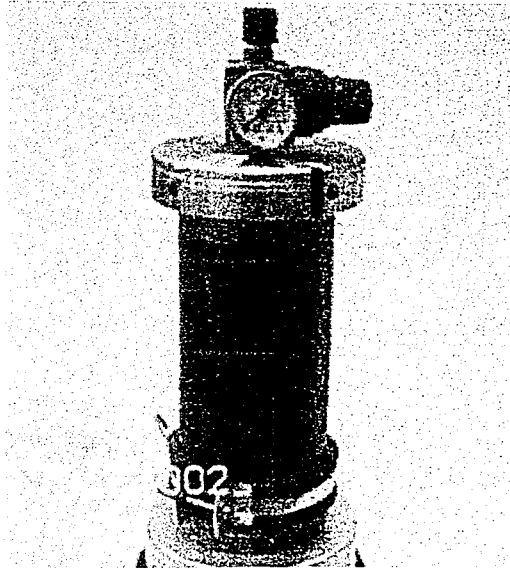
Figure 6.1. Pressure chamber with pressure regulator and pressure gauge

Material:
Aluminum
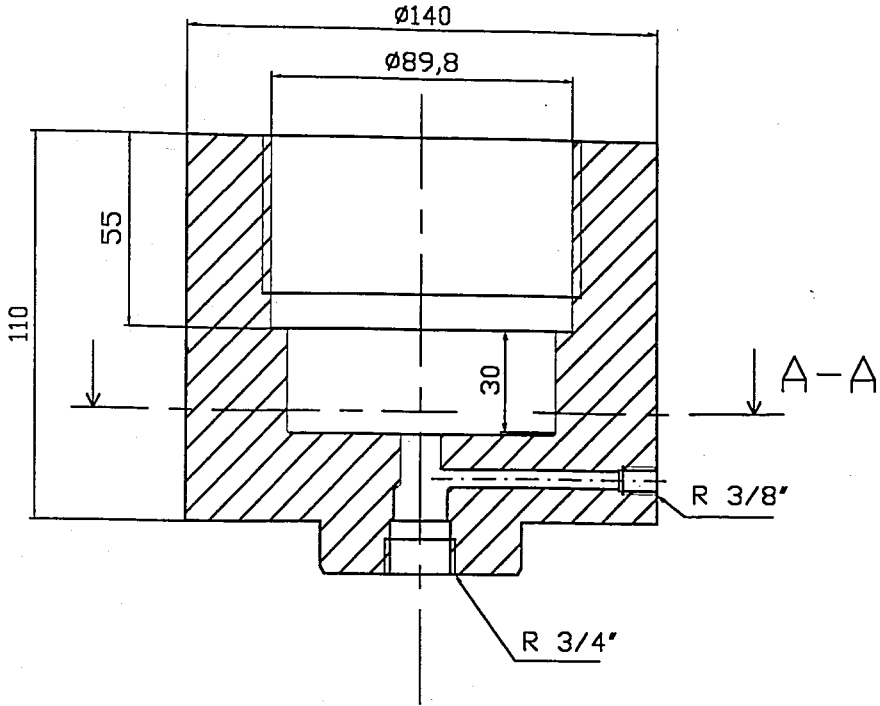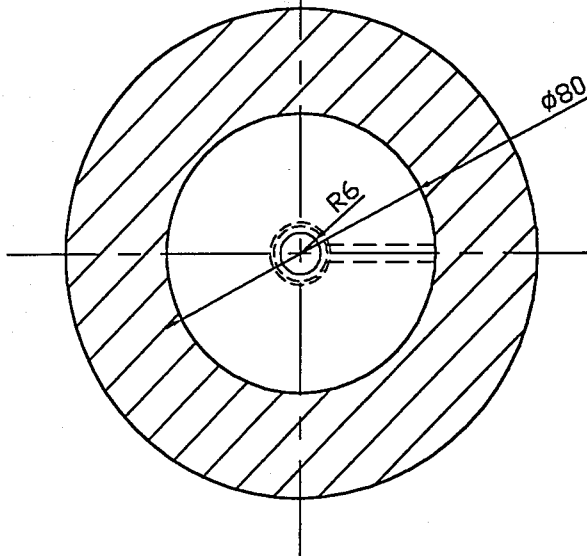
Figure 6.2. Aluminum bottom part with channels and mold housing

6.3. Image Processing

Images obtained at a chosen magnification are used to measure the porosity, the pore width, and the pore width distribution of the plastic mold. The samples from specimens were viewed under the microscope and the image of the desired area is transferred to the computer using a video camera through the frame-grabber card. The image is acquired as a 256 gray-level image. Normal preparative procedures for SEM microscope were not followed because the microscope used was an ESEM microscope, Phillips XL 30 ESEM.

Organic samples such as polymers have low electron emissivity and poor thermal and electrical conductivity, are radiation sensitive, and, unlike biological materials, have relatively few active ligand binding sites which could accommodate specific chemical stains. Placing polymer samples directly into a SEM will result in the sample building up a charge as the electron beam scans it. At some point this charge will interact with the incident beam and result in image distortion. Another problem and perhaps more serious and limiting is radiation damage as a result of the electron beam interacting with the polymer. This severely restricts the conditions under which the polymer sample may be examined i.e. low accelerating voltage and beam current with a resulting low resolution. Therefore in SEM analysis polymers are generally coated with an electrically conductive material, usually with gold or platinum. However, by environmental scanning electron microscope no additional work is needed. Samples are simply cut from the specimens put on stubs and viewed. The morphology and particle diameter (d_s) of the polymer powders used in molds can be seen in Figure 6.3. The sample was prepared from specimen 4. 40 and 100 μm spherical polymer powders were used in this specimen.

In Section 6.2 the average particle size of the powders in the mold was calculated as 94 μm. Figure 6.3 shows finer particles. In permeability tests the liquid passes through the voids of the mold. If relatively larger pores are present in the medium the liquid will flow faster through these pores. This may be one of the reason of the deviation in the calculated particle size from permeability values.
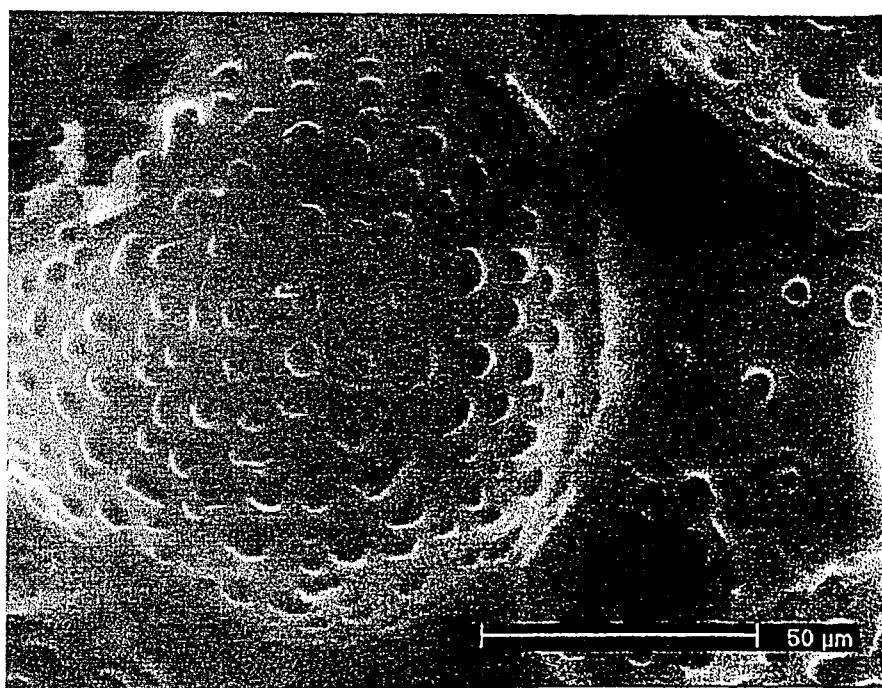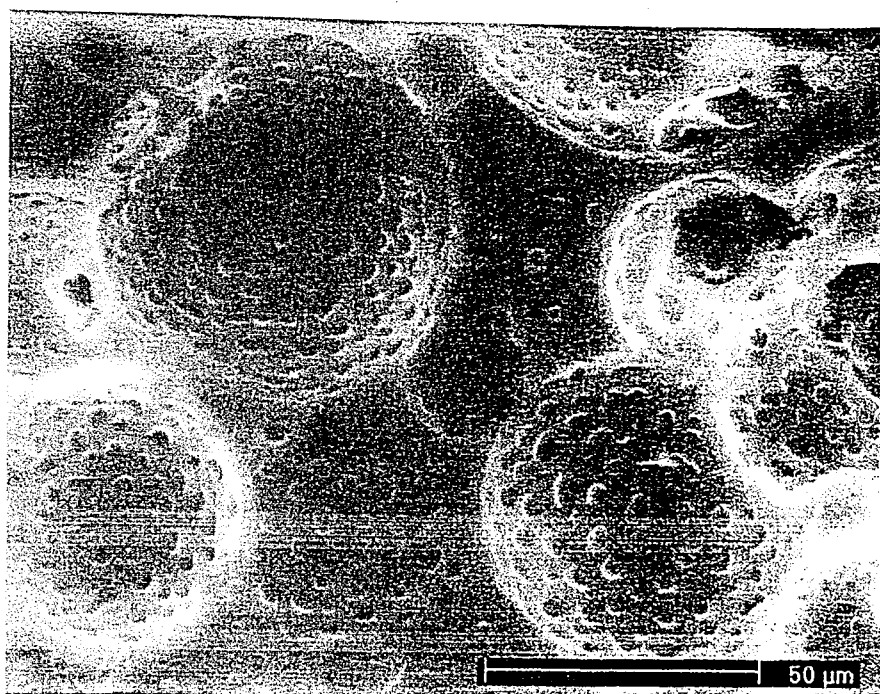
Figure 6.3. Polymer powders in specimen 4

The images, obtained from each sample were composed of 256 gray levels. For measuring the pore width images were binarized at a chosen threshold level T. The pores are in black and the surface of the mold is white. The analysis of the binarized image is based on digitalization of each pore of the mold surface followed by measurement of the pore width. The dispersion of the pore width is given as histograms and a mean pore width is also shown.

The image taken from specimen 3 is shown in Figure 6.4. The particle size of the polymer powder used in this specimen was 100 μm.

After adjusting the contrast level of the image a filter was applied to sharpen the edges of the image. The pores are distinguished from the background by selecting a range of the gray levels. This is done by selecting a certain threshold level, resulting in a binary image. Threshold level of specimen 3 is 30. Resultant image is shown in Figure 6.5.
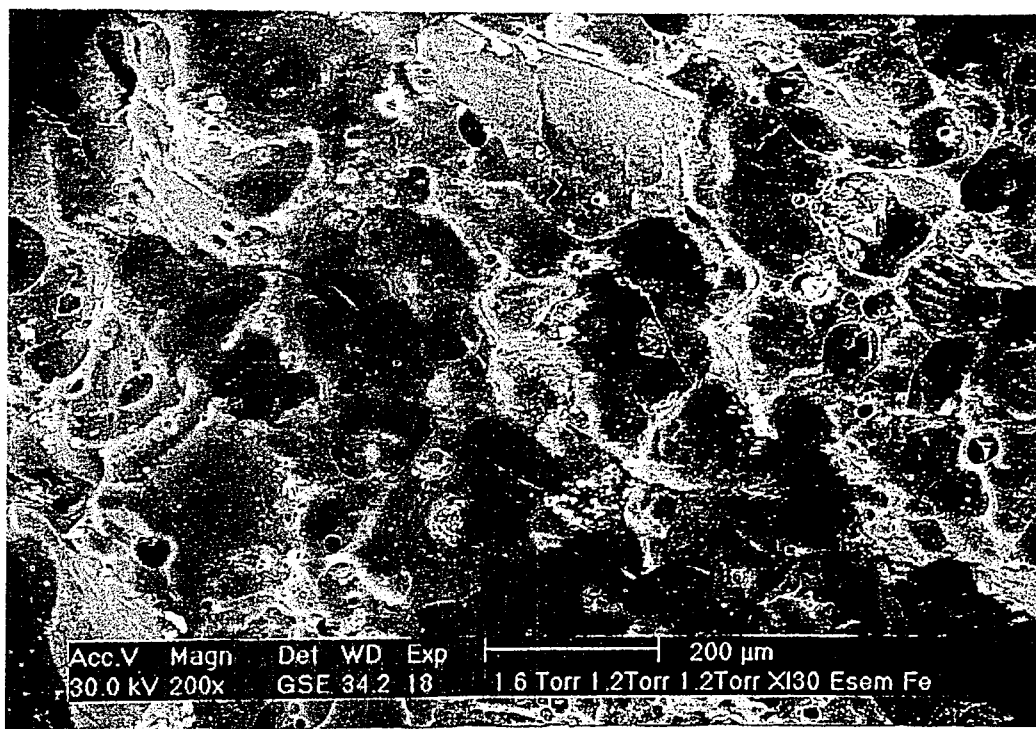
Figure 6.4. The image of the sample taken from specimen 3
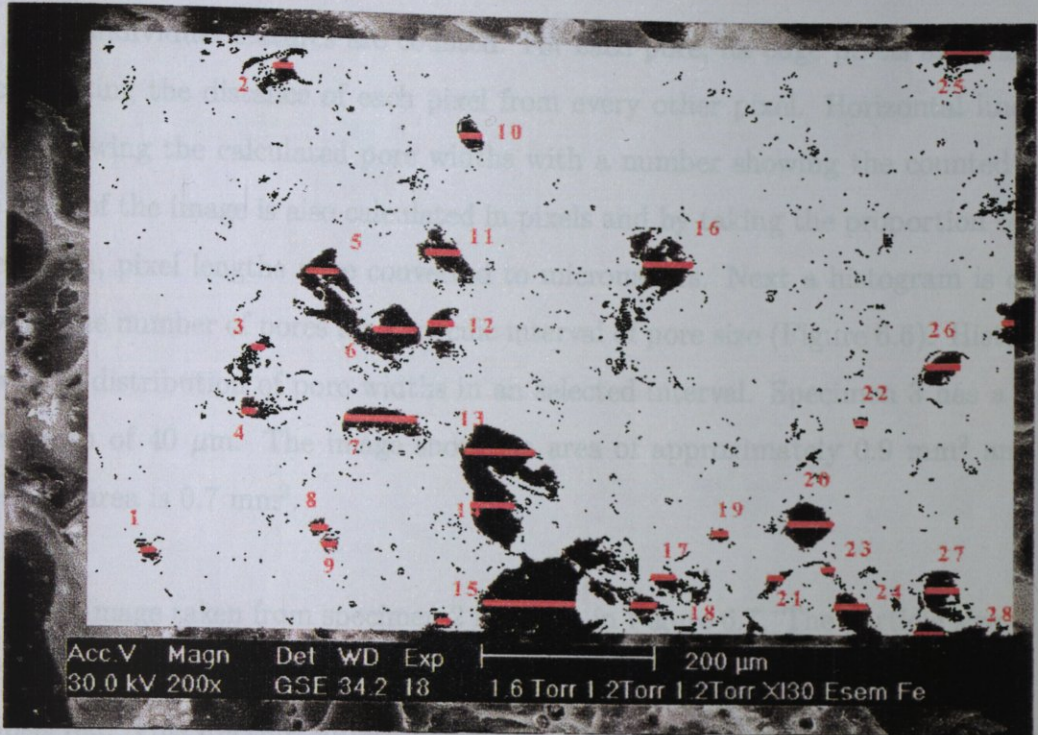
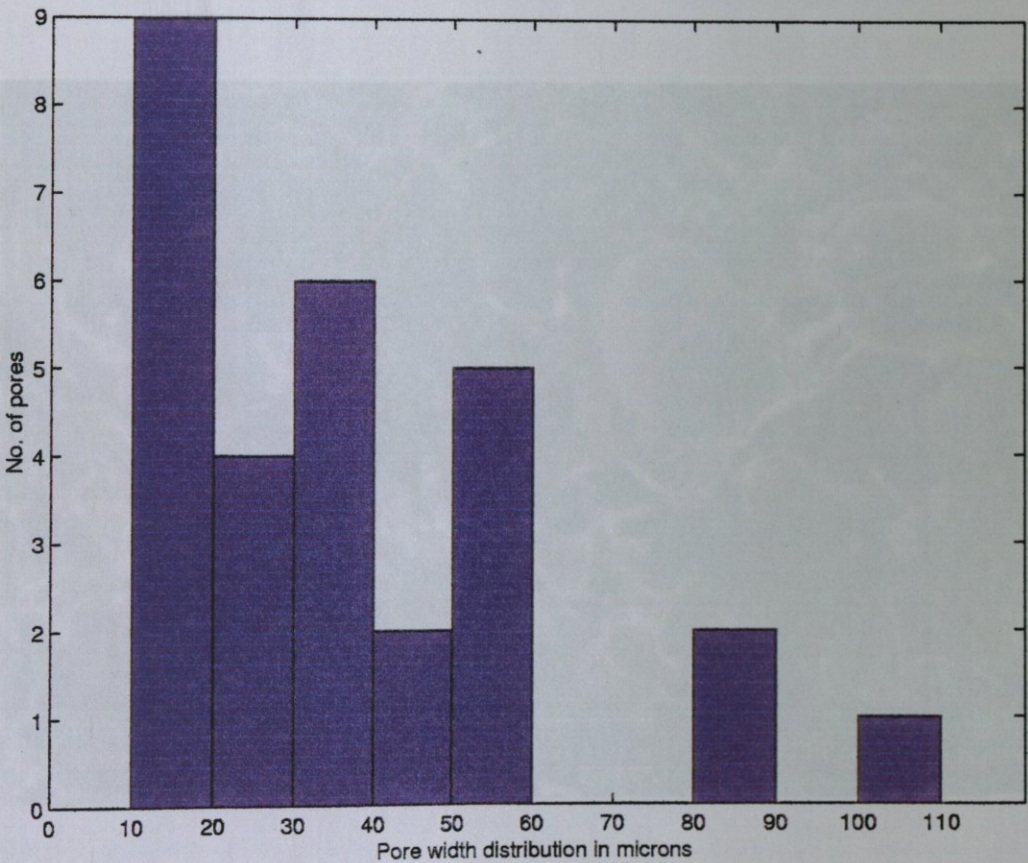Figure 6.5. Detection of pore widths of specimen 3 by threshold

Figure 6.6. Histogram showing the pore width distribution for specimen 3

The individual features are counted. For each pore, its edge pixels are analyzed by computing the distance of each pixel from every other pixel. Horizontal lines are drawn showing the calculated pore widths with a number showing the counted pore. The scale of the image is also calculated in pixels and by taking the proportion of each pore width, pixel lengths were converted to micrometers. Next a histogram is drawn showing the number of pores for a specific interval of pore size (Figure 6.6). Histogram shows the distribution of pore widths in an selected interval. Specimen 3 has a mean pore width of 40 μm. The image shows an area of approximately 0.9 mm^2 and the threshold area is 0.7 mm^2.

The image taken from specimen 2 is shown in Figure 6.7. The particle size of the polymer powder used in this specimen was 60 μm. In the figure polymer powders can be observed. This fracture surface image also shows a void which is probably a result of the separation of the powder from the adjacent layer. The procedures applied are the same and the resultant binarized image is shown in Figure 6.8.

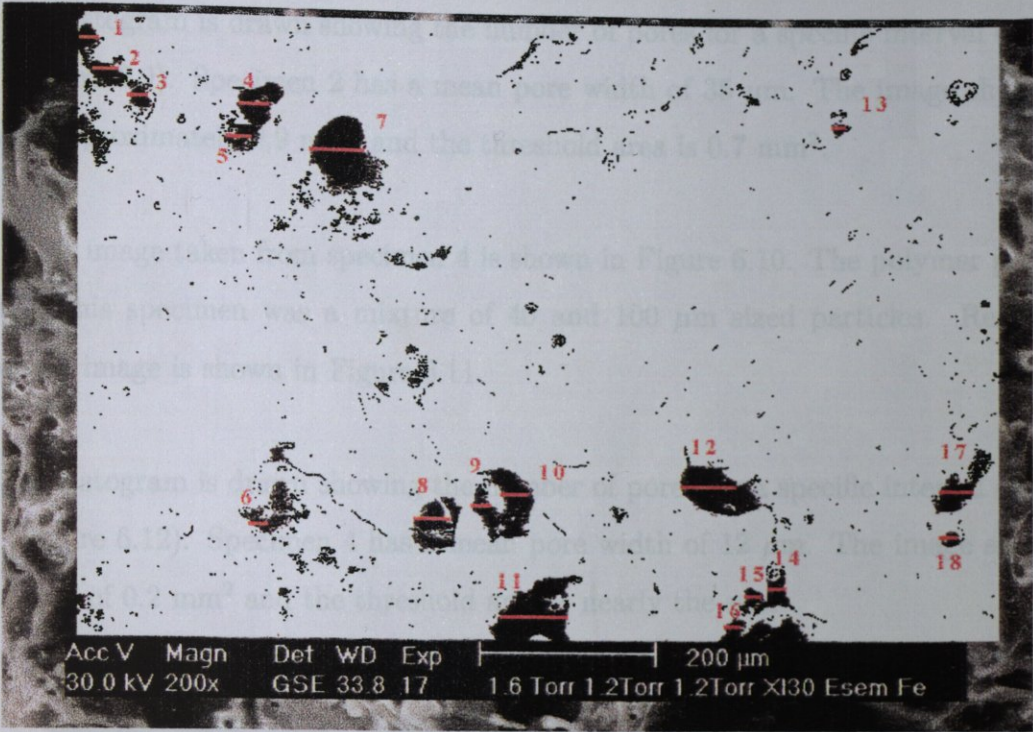Figure 6.7. The image of the sample taken from specimen 2

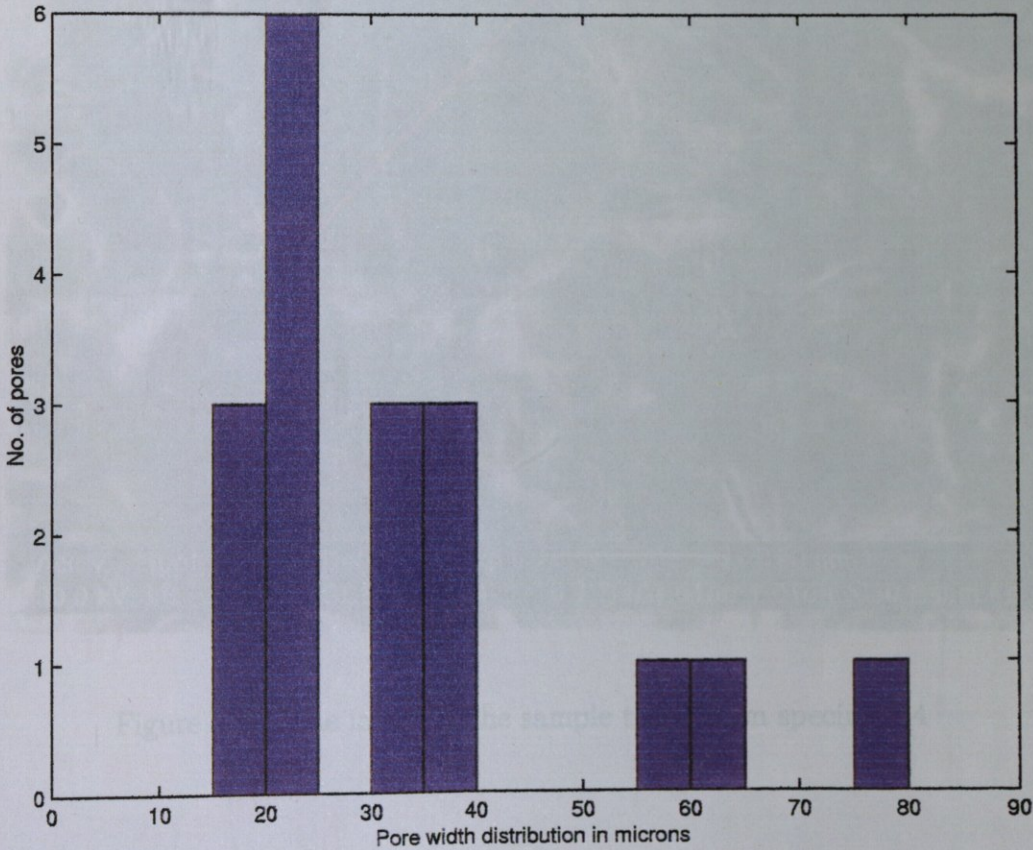Figure 6.8. Detection of pore widths of specimen 2 by threshold

Figure 6.9. Histogram showing the pore width distribution of specimen 2

A histogram is drawn showing the number of pores for a specific interval of pore size (Figure 6.9). Specimen 2 has a mean pore width of 35 μm. The image shows an area of approximately 0.9 mm^2 and the threshold area is 0.7 mm^2.

The image taken from specimen 4 is shown in Figure 6.10. The polymer powder used in this specimen was a mixture of 40 and 100 μm sized particles. Resultant threshold image is shown in Figure 6.11.

A histogram is drawn showing the number of pores for a specific interval of pore size (Figure 6.12). Specimen 4 has a mean pore width of 12 μm. The image shows a total area of 0.2 mm^2 and the threshold area is nearly the same.
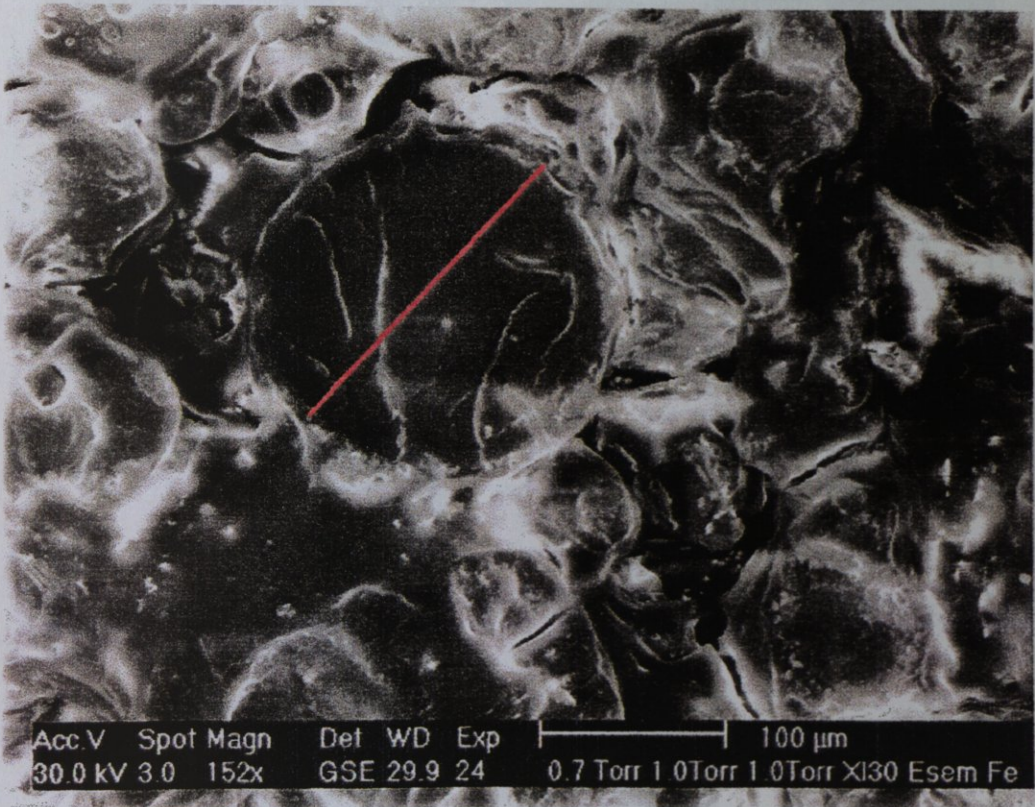

Figure 6.10. The image of the sample taken from specimen 4

These images show that the size and size distribution or grading of the spherical polymer particles are largely decisive to the final pore size and pore structure.
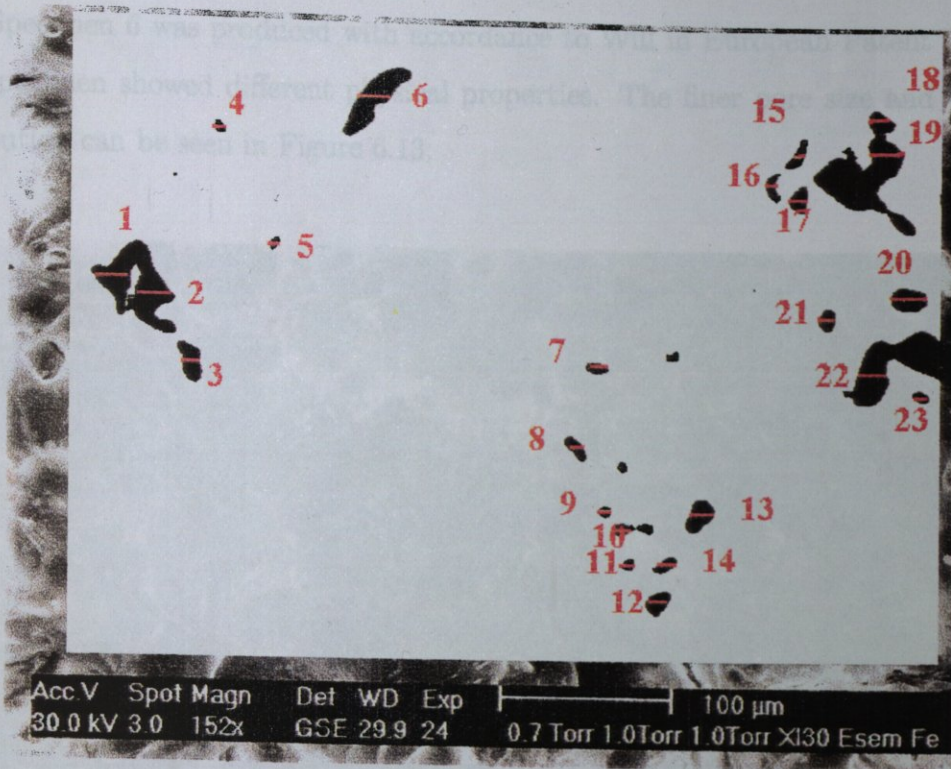
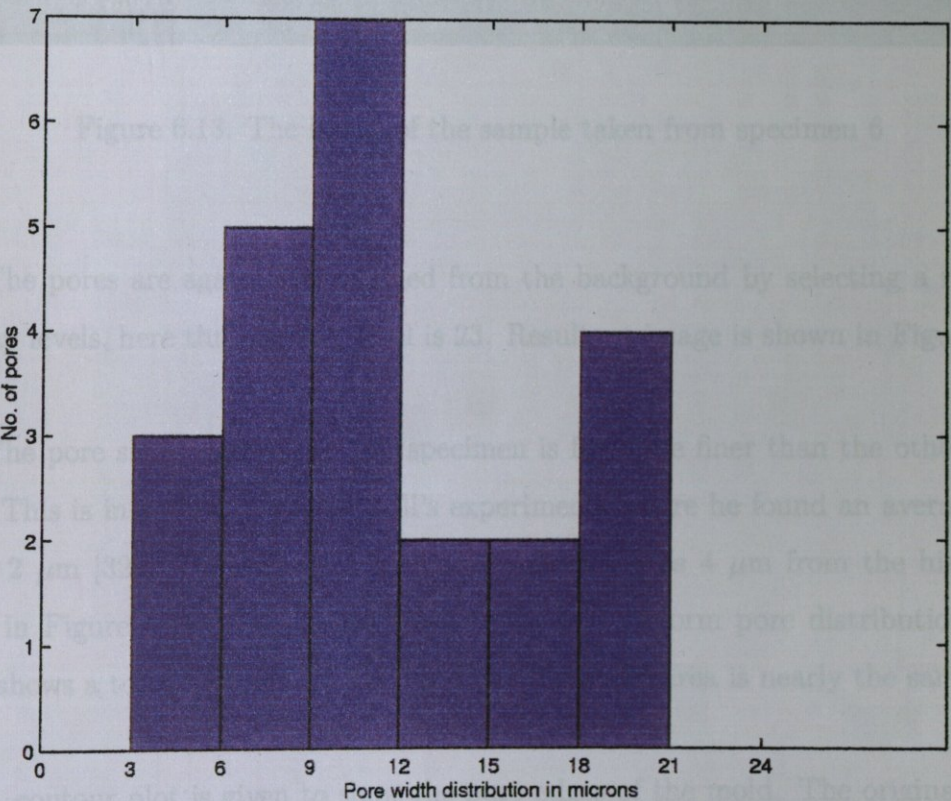Figure 6.11. Detection of pore widths of specimen 4 by threshold

Figure 6.12. Histogram showing the pore width distribution of specimen 4

Specimen 6 was produced with accordance to Will in European Patent 516,224. This specimen showed different physical properties. The finer pore size and uniform distribution can be seen in Figure 6.13.
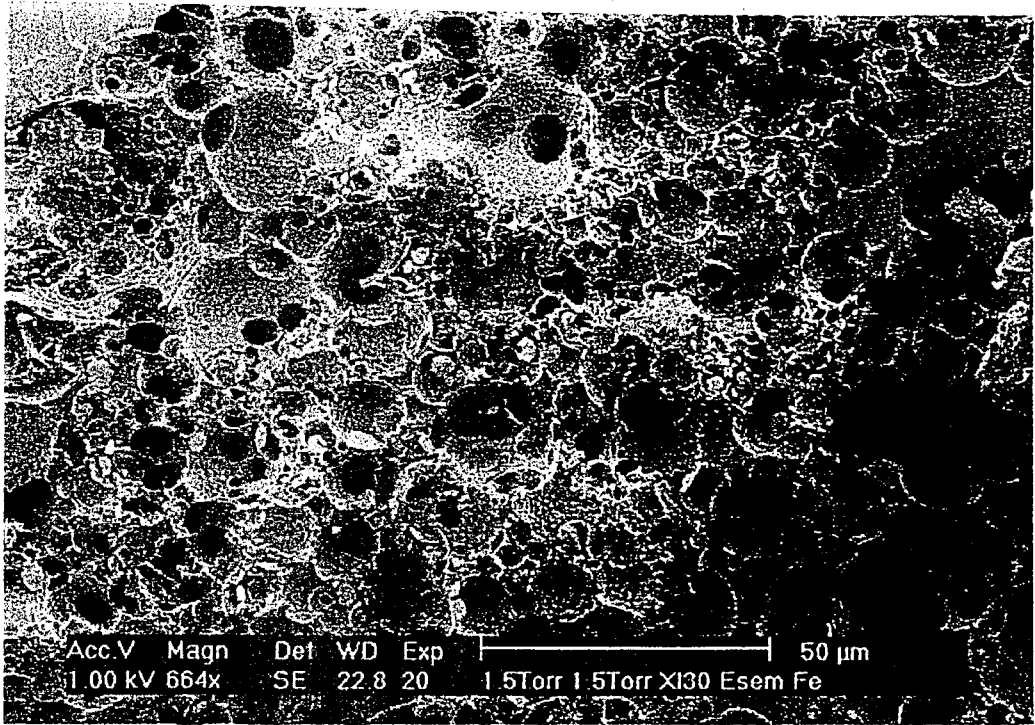

Figure 6.13. The image of the sample taken from specimen 6

The pores are again distinguished from the background by selecting a range of the gray levels, here thresholding level is 23. Resultant image is shown in Figure 6.14.

The pore sizes observed in this specimen is far more finer than the other specimens. This is in accordance with Will's experiments where he found an average pore size of 2 μm [32]. The average pore size is calculated as 4 μm from the histogram shown in Figure 6.15. This specimen also shows a uniform pore distribution. The image shows a total area of 0.02 mm^2 and the threshold area is nearly the same.

A contour plot is given to show the pore edges of the mold. The original image was sliced to form six parts of contoured images. Matlab Image Processing Toolbox^{TM} is used for obtaining the contour plot (Figure 6.16).
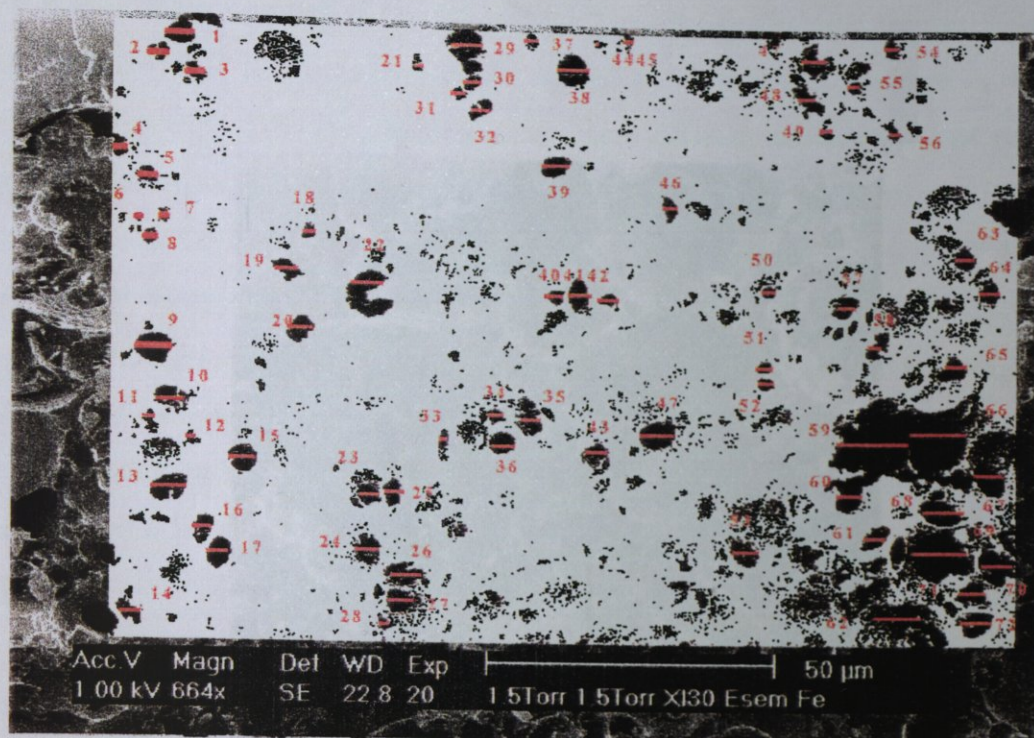
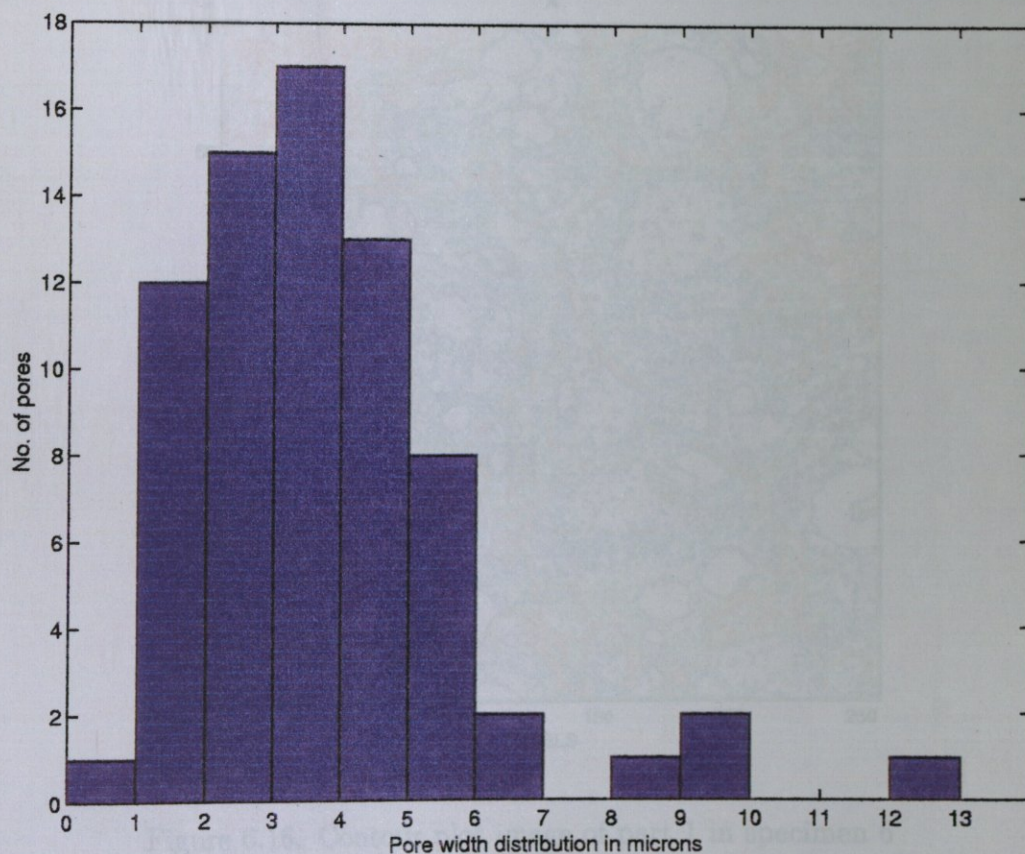Figure 6.14. Detection of pore widths of specimen 6 by threshold

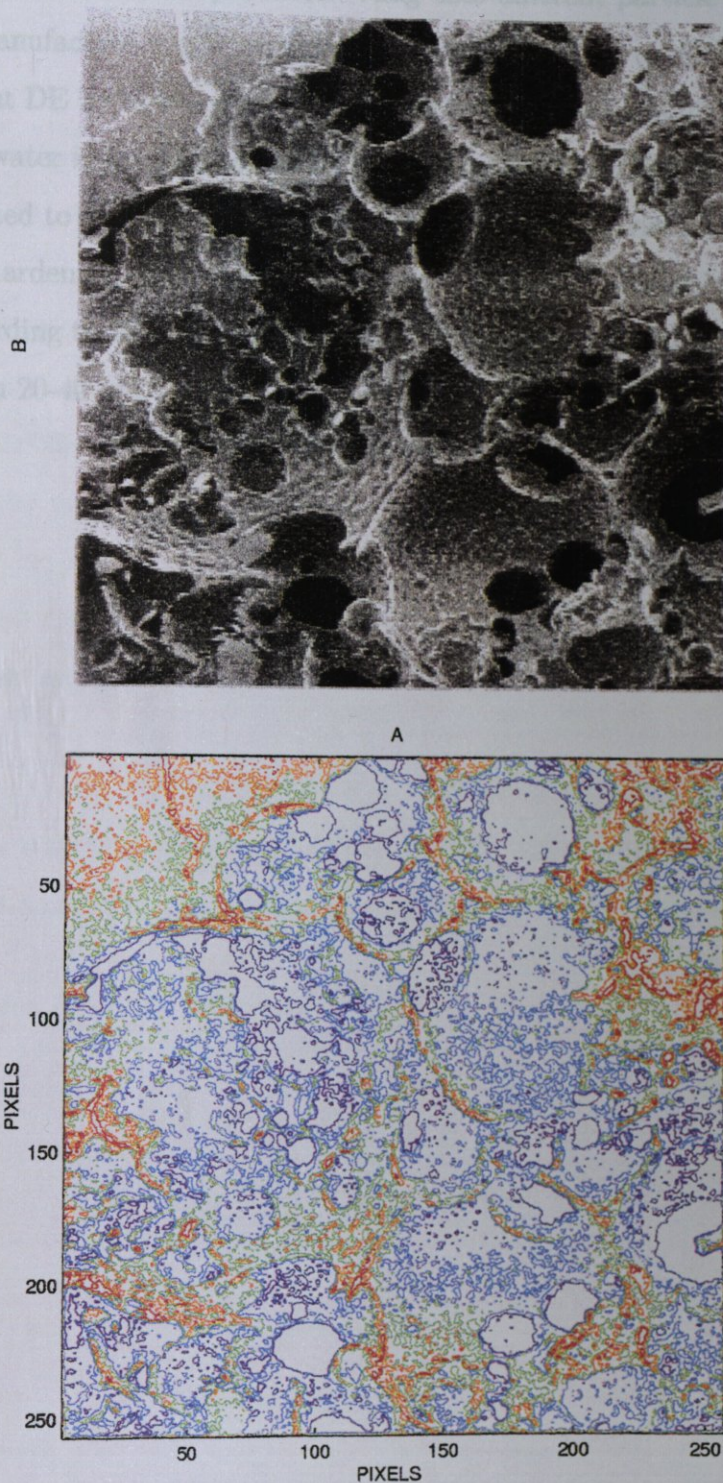Figure 6.15. Histogram showing the pore width distribution for specimen 6

Figure 6.16. Contour plot image of part 1 in specimen 6

Within the framework of the experiments, in accordance with the procedure of Jung [26] and Will [32], mold materials usable, either without pressure or with a pressure of up to 4 MPa, are produced. Jung uses different particle sizes of polymer powders to manufacture molds with average pore sizes of 20 to 40 μm. Will also in German Patent DE 1,928,026 uses a similar method. In US 5,033,950 and EP 516,224 however, the water in oil emulsion either with or without the addition of a dispersing agent is adjusted to a degree of dispersion or a corresponding viscosity such that after molding and hardening, pore widths of between 1 and 5 μm are achieved. Specimen 6 prepared according to Will showed a similar property while other specimens pore sizes varied between 20-40 μm.

7. CONCLUSIONS

In order to understand the mold characteristics the theory of filtration and filter medium properties is studied. Slip casting process is basically a filtration process, so filtration knowledge is applicable. The process is further extended by using appropriate molds to pressure application.

Appropriate mold means a mold with high porosity and good permeability to allow the filtrate to pass through and collect the solid on its surface. In slip casting filtrate is water and the solid body consolidated at mold's surface is the product. By using acrylic polymer powders a porous, and permeable mold is manufactured. The pore sizes hence permeability is adjusted by using different particle sizes of these powders. The achieved pore sizes are 20-40 μm. These molds can be used in high pressure slip casting applications.

Another method is subjecting a water in oil emulsion to hardening. Using this method, molds with finer pores and less permeability are manufactured. The achieved pore sizes are 3-5 μm. These molds can be used in low pressure slip casting applications.

APPENDIX A: CONTOUR IMAGES SHOWING PORES IN SPECIMEN 6

Image Processing Toolbox^{TM} of Matlab was used to obtain the contour images of specimen 6. The images give surface characteristics of the sample. Pores, edges and holes are observed.
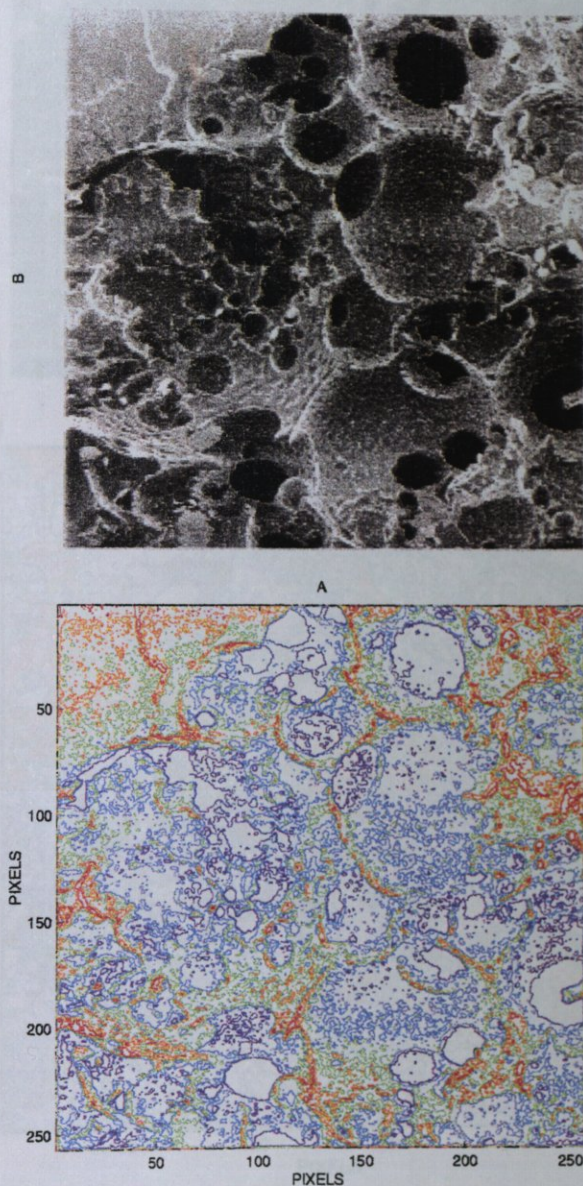

Figure A.1. Contour plot image of part 1 in specimen 6
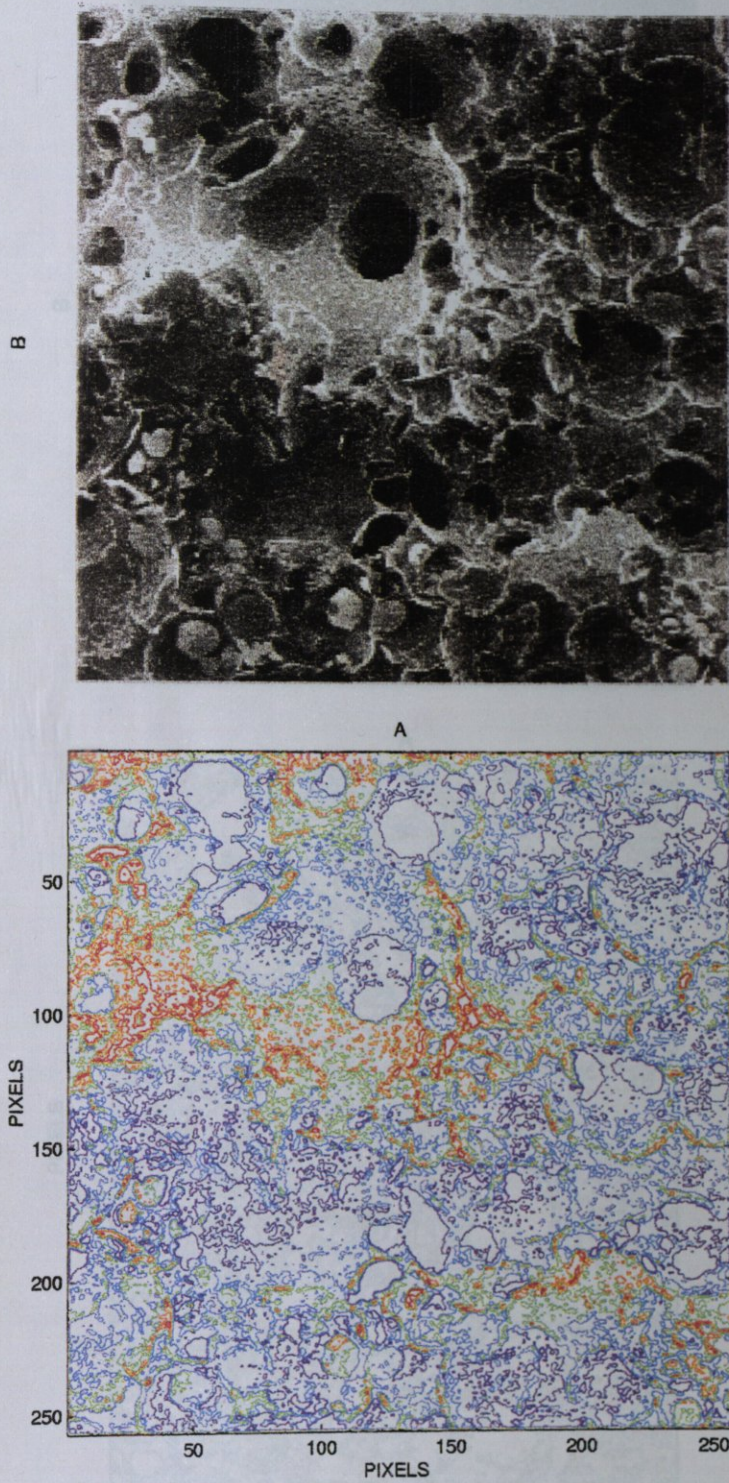
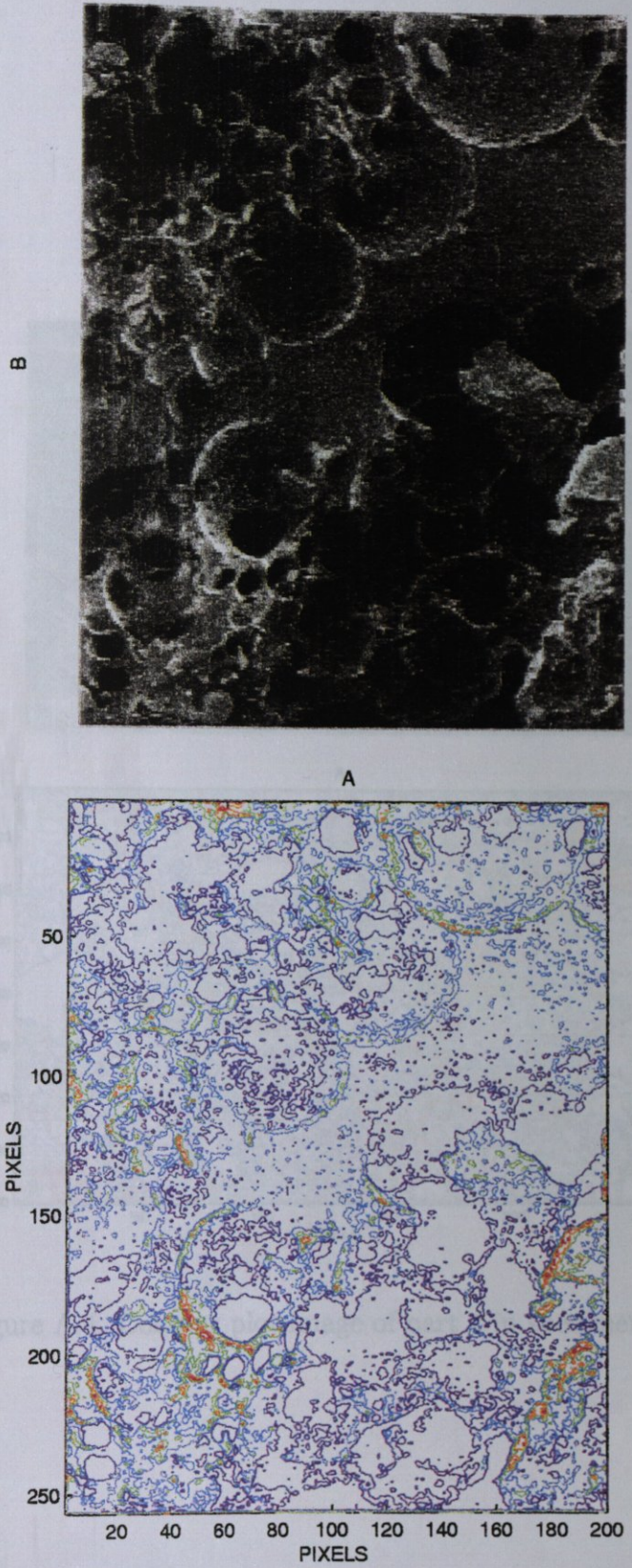Figure A.2. Contour plot image of part 2 in specimen 6

Figure A.3. Contour plot image of part 3 in specimen 6

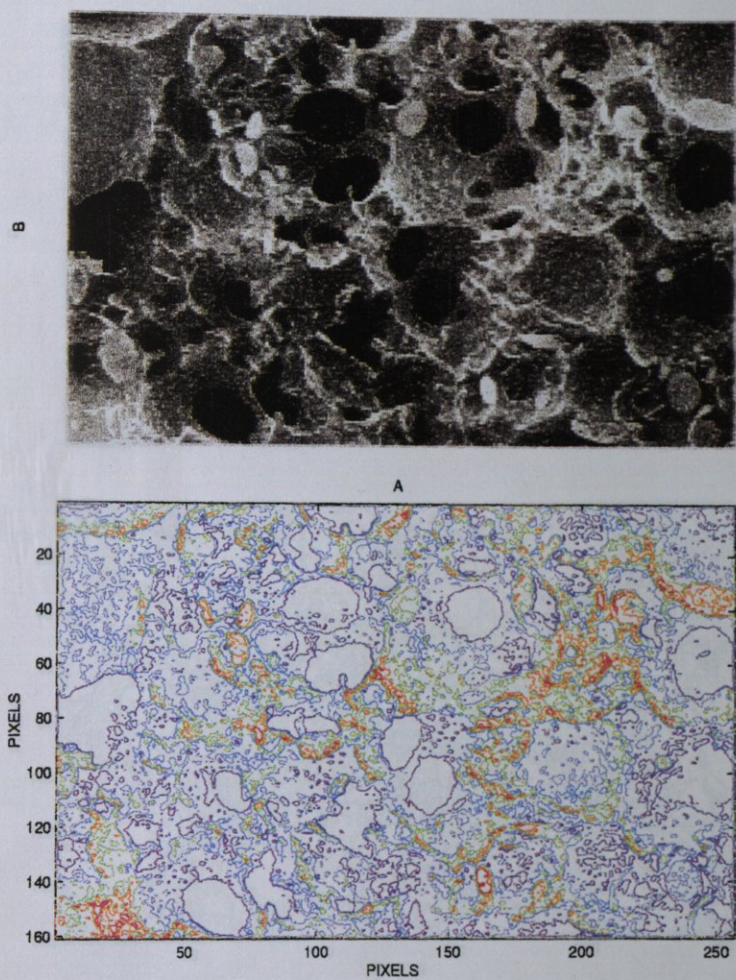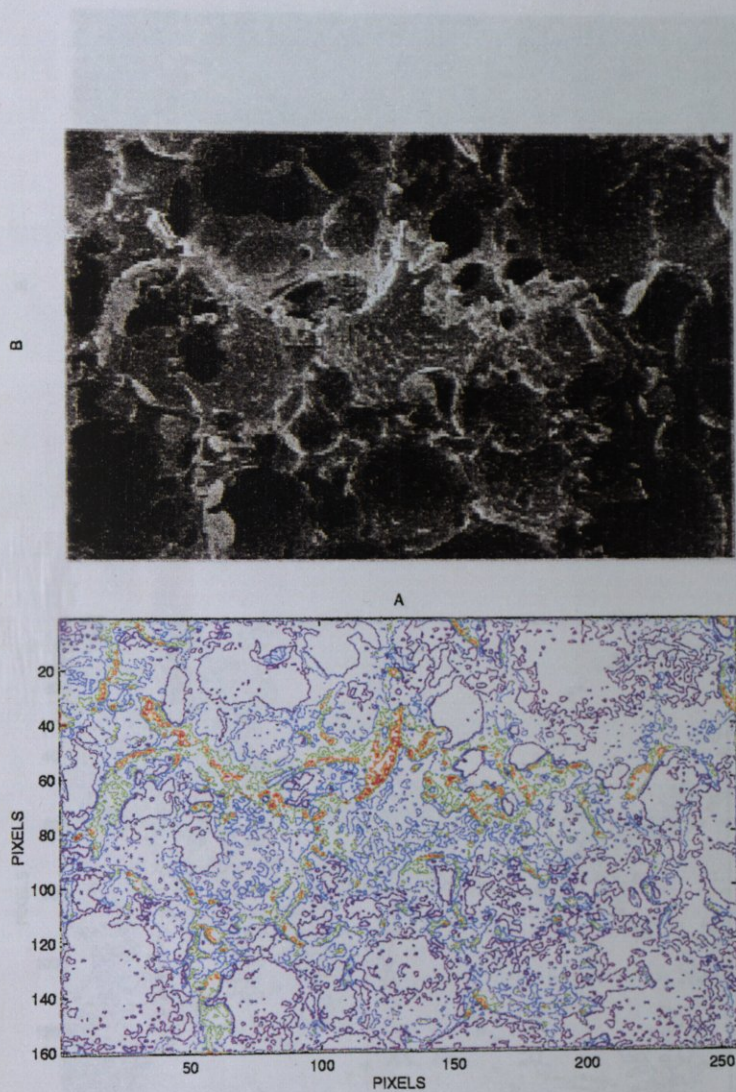Figure A.4. Contour plot image of part 4 in specimen 6

Figure A.5. Contour plot image of part 5 in specimen 6

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