PRACTICAL OBSERVATION OF DEVIATION FROM LUCAS-WASHBURN SCALING IN POROUS MEDIA

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ABSTRACT

This work analyses the applicability of the Lucas-Washburn equation to experimental observations of imbibition into real network structures. The experimental pore structures used in this study are constructed from tablets of two finely ground calcium carbonates, with defined differences in particle size distribution. These are compressed under a range of different applied pressures to achieve a controlled series of porosities while maintaining the surface chemical, particulate and morphological pore characteristics constant. The porosities are determined by mercury intrusion porosimetry applying corrections for mercury compression and penetrometer expansion together with a correction for sample skeletal compression [7]. Imbibition studies are made by bringing each porous sample into contact

with a supersource of liquid and the dynamic imbibition is recorded gravimetrically. Results follow a long timescale macroscopic absorption rate depending on the square root of time but show a failure to scale according to pore size in the Lucas-Washburn equation even though the constants of surface energy, contact angle and fluid viscosity have been maintained. Furthermore, values of average measured pore radius are shown to be finer than the Lucas-Washburn predicted equivalent hydraulic capillary radius. The predominance of a relevant pore size within a given pore size distribution forming a selective pathway filling based on inertial retardation of larger pores and short-term linear time wetting in finer pores is argued to account for the departure from simple pore size scaling.

Keywords: porous media, imbibition, hydraulic radius, Lucas-Washburn, capillarity, inertial wetting.

INTRODUCTION

The imbibition of a wetting liquid into a porous structure is a frequently occurring phenomenon in both natural and industrial systems. The stimuli for the work presented here come from the paper and printing industries where imbibition processes are crucially responsible for final product quality. More precisely, the imbibition dynamics of an offset ink vehicle, consisting mainly of low viscosity mineral oils, into a paper coating structure is the focus of interest. The coating layer is mainly formed by fine mineral pigment particles, today frequently consisting of calcium carbonate.

Despite many studies in other fields of surface chemistry having identified some limitations of the well known Lucas-Washburn equation when applied to the imbibition of liquid into porous substrates [1-5] it is still frequently used, especially in the field of paper science. In this paper we present new results, using an experimental technique, described earlier [6], which is used to sample directly the mass uptake of fluid into a macroscopic consolidated structure of finely ground calcium carbonate. This technique is used to investigate the imbibition of a mineral oil ($\sim C_{16}$-fraction) into structures over a range of different porosities, each determined independently by mercury porosimetry adopting the required specially developed compression correction algorithms [7]. The important aspect of this work is that we maintain the surface chemical and overall geometrical similarity of the samples. Often, these features are either overlooked or, conversely, assumed to be changing when correlating the absorption dynamic between different porosity samples in an attempt to support the continued validity of Lucas-Washburn.

THEORETICAL BACKGROUND

An early approach to analyse imbibition is reported by Bell and Cameron [16] who find a root dependency of t for imbibition which was apparently found independently also by Ostwald in 1908 [11]. Lucas experimented with glass tubes and filter-papers to verify the equation he obtained combining the Laplace relation with Poiseuille's equation of laminar flow [11]. His focus was mainly to fortify the *square* root dependency of t. Washburn [12], not being aware of Lucas' work, performing vertical and horizontal capillary experiments, derived the same equation as Lucas and discussed slip behaviour and the limits of Poiseuille flow at both ends of the liquid column and the equation's applicability to porous substrates. The main drawback of the combined Lucas-Washburn approach is the lack of inertial terms, relating to the mass of fluid under motion, as was recognised by Rideal [17]. Bosanquet complemented Rideal's solution in 1923 [10], adding the inertial impulse drag effect associated with an accelerating fluid. Later, several researchers, for example Szekely et al [18], being only partially aware of the mentioned classical work, found solutions similar to Bosanquet's equation adding other (minor) correction terms.

In previous studies we investigated the mechanism of absorption of polar liquids into coating pigment structures [8], [9]. We identified the potential relevance of inertial flow as physically predicted by Bosanquet [10], who expanded the well-known Lucas-Washburn [11, 12] equation to contain the inertial effect of the liquid mass which has to be accelerated by the wetting force. According to the solution of Bosanquet, there exists a time-dependent optimum for flow rate as a function of capillary radius, liquid density and viscosity. The consequence is that pores up to a given diameter in a porous network, this diameter in turn increasing as a function of time, fill very fast while larger features remain by-passed and tend to remain unfilled under conditions of limited supply volumes of fluid, as is the case with thinly applied ink films or droplets. This promotes a preferential pathway flow. Both phenomena, inertial

flow and unfilled pores, have been observed and analysed. Inertial flow in a glass capillary, following initially a linear relation with time, was observed directly by Quéré using a high speed camera [13]. The existence of unfilled or by-passed pores is known from soil science and studies made using micro models [14]. The experimental method we use provides no direct knowledge about the initial regime of uptake due to the equilibration of the contact forces and experimental resolution over this timescale. Hence it is not possible to determine the expected linear time relation for purely inertial wetting at the time of initial contact.

To illustrate these combined issues in relation to a network structure, we previously applied a modified Bosanquet equation to a sequential wetting algorithm for Newtonian fluids in a unit cell-based pore space simulator, Pore-Cor[1] [8]. It could be seen that in each single feature of a porous network, where the liquid becomes accelerated, inertia acts over a timescale similar to the pore filling time for the finer pores encountered in paper coatings and leads to a differential in wetting front velocity and position during absorption between the finer and the larger pores. At the present stage, the size of the network simulator unit cell and the computer processing time still limit direct comparison with longer term experimentation. In our earlier approach [8], a scaling function was used to extrapolate the initial regime of simulated imbibition of the unit cell where the slope of the uptake curve matches experimental data. Interestingly, on a macroscopic scale a proportionality with respect to the square root of time is once again observed due to mass balance criteria. This systematically supports the reasoning why the long-assumed experimental verification of Poiseuille flow, and hence Lucas-Washburn dynamics, has been accepted, with, however, the remaining need for a defined effective capillary radius or surface energy relationship to describe the discrepancy between absorption rates for fine and coarse structures. This issue is discussed further and

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[1] Pore Cor is a software program developed by the Environmental and Fluid Modelling Group, University of Plymouth PL4 8AA, U.K.

modelled in some detail in a recent publication by Ridgway and Gane [15]. The relevance of considering inertial wetting as a sequential process at the intersection nodes of a network structure containing a range of pore sizes is well-illustrated by this modelling method.

In practical applications many recent researchers considered the impact of inertia on imbibition to be negligible due to its relevance only during short time (initial) imbibition. This may be true for imbibition into a long single capillary and for some liquids. Only a few workers in the field recognised the potential summing effect of inertia in the interconnected void network of a real porous substrate. Sorbie et al [19] showed the selective mechanism of inertia-retarded flow using a pore-doublet model and by applying Szekely's equation. High liquid viscosities shift the time of inertial flow into even shorter timescales and low densities decrease the effect of inertial retardation. Even if inertia is manifest, macroscopically a $\sqrt{t}$ behaviour may still be observed from a network structure. Thus, concluding that a $\sqrt{t}$ behaviour means that inertia plays no role is wrong. In this respect the picture of a single capillary representing a porous substrate is misleading. While in a capillary the inertial regime is relevant only in the initial extremely short time frame of absorption, in a porous network there is an inertial contribution each time the liquid is accelerated. These acceleration events, sometimes observed in the most extreme cases as Haines-jumps, are well-known and observable microscopically. The contribution of inertia, therefore, is in terms of a "decision-making process" governing which pores fill and which stay only partially filled. The $\sqrt{t}$ behaviour shows only that viscosity controls the absorption over the remaining timescale once the decision of which pore will fill is made.

Einset [20] compared imbibition rates of different liquids into particulate structures of carbon and silicon carbide which were characterised by mercury porosimetry. The Lucas-Washburn equation is used to describe the parabolic distance in time, but a discrepancy (1-2 orders of

magnitude) was found comparing the obtained pore radii with those of mercury porosimetry. This was explained by an apparent network effect and assumed variation of contact angles induced by contaminations. Li, Giese et al. [21] used a variety of alkanes for wicking experiments into ceramic structures. They assumed a contact angle of zero, and found an effective radius which was smaller than that afforded by mercury porosimetry by a factor of about 2. They questioned the mercury porosimetry result. Our opinion is that mercury porosimetry has shown its reliability with many structures of high bulk moduli and its reliability was confirmed also in our previous work using saturation wetting liquid imbibition methods [6].

MATERIALS

We chose two commercially available dry powder products, both derived from natural calcium carbonate, ground under similar chemical conditions from the same Orgon, France, limestone source. The grinding is made in a wet state at consistent solids content using a polyacrylate dispersing agent applied in proportion to the specific surface area of the final pigment size distribution and subsequently dried. To avoid the interference of dispersant molecular weight and size in relation to the pigment size, the two size distributions of the respective products were chosen to be only slightly different in respect to the quantity of particles less than the 2 µm Stokesian equivalent hydraulic diameter, being 90 % w/w < 2 µm and 95 % w/w < 2 µm, defined as "coarse $CaCO_3$" and "fine $CaCO_3$", respectively. The cumulative particle size distribution curves of the two materials, as measured by sedimentation[2], are shown in Fig. 1.

The bulk samples used in this work are cuboid blocks of each ground pigment, compacted over a range of pressures to form a series of well-defined porosities. The detailed method of

powder compaction, applying pressures up to ~ 260 MPa in a steel die on an hydraulic press and subsequent sample grinding, is described elsewhere [6]. It proved to give a reproducible and relatively homogeneous porous structure. Such homogeneity is a prequisite so that specimens from the same sample can be used independently for the fluid imbibition and mercury porosimetry experiments. The porosity range achievable with the coarse powder was found to be much broader (~ 20-40 %) than the range achievable with the fine pigment (~ 26-33 %), indicating differences in packing characteristics. The samples, being consolidated and maintaining their integrity, did not require a sample vessel for the fluid imbibition experiments, thus eliminating uncertainties of fluid interactions between the sample and such a vessel.

To reduce artefacts caused by the wetting of their outer surfaces, the samples were coated with a thin barrier line of a silicone polymer[3] around the base of the vertical edges arising from the basal plane. The remainder of the outer planes were not coated to allow for the free movement of displaced air during liquid imbibition, and to minimise any interaction between the silicone and the absorbed liquid.

The liquid used was a mineral oil[4] (aromatic free quality), as employed typically in the formulation of offset printing inks. The contact angle of oil/calcium carbonate, q, was assumed to be zero following the data of Chibowski et al. [22], who have shown that aliphatic alkanes completely wet a number of mineral surfaces including calcium carbonate - this being the basis upon which these authors used alkanes to determine an effective pore radius. Additionally, this wetting behaviour was also confirmed by observing the complete spreading of an oil droplet on a dispersant pre-adsorbed macro-crystal surface of calcium carbonate. An

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oil viscosity of 4.3 mPas was determined with a StressTech rheometer performing a small ramp of shear rates showing Newtonian behaviour. The surface tension was measured to be 27.4 mNm^{-1} by the means of a Krüss Digital Tensiometer K10T. The density of 0.805 gcm^{-3} was given by the manufacturer. These values indicate that it can be assumed to be an alkane isomeric blend of around C_{16}.

MERCURY POROSIMETRY

Each structure used for the experimentation was analysed independently with mercury porosimetry. A Micromeritics Autopore III mercury porosimeter was used to measure the intrusion characteristics of the samples. The maximum applied pressure of mercury was 414 MPa (60 000 psia), equivalent to a Laplace throat diameter of 0.004 µm. Small samples were used, each of around 1.5 g in weight. The equilibration time at each of the increasing applied pressures of mercury was set to 60 seconds. The mercury intrusion measurements were corrected for the compression of mercury, expansion of the glass sample chamber or 'penetrometer' and compressibility of the solid phase of the sample by use of the following equation from Gane et al. [7], as incorporated in the software Pore-Comp [5].

$$V_{\mathrm{int}} = V_{\mathrm{obs}} - \boldsymbol{d}V_{\mathrm{blank}} + \left[0.175(V^{\mathrm{I}}_{bulk}) \log_{10}\left(1 + \frac{P}{1820} \right) \right] - V^{\mathrm{I}}_{bulk}(1 - \Phi^{\mathrm{I}})\left(1 - \exp\left[\frac{(P^{\mathrm{I}} - P)}{M_{\mathrm{ss}}} \right] \right) \quad (1)$$

where V_{int} is the volume of intrusion into the sample, V_{obs} the intruded mercury volume reading, $\boldsymbol{d}V_{\mathrm{blank}}$ the change in the blank run volume reading, $V^{\mathrm{I}}_{\mathrm{bulk}}$ the sample bulk volume at atmospheric pressure, P the applied pressure, Φ^{I} the porosity at atmospheric pressure, P^{I} the atmospheric pressure and M_{ss} the bulk modulus of the solid sample. The volume of mercury intruded at the maximum pressure, once corrected for sample compression effects, can be used to calculate the porosity of the sample. For convenience, a representative pore radius is

defined as $r_{50} = d_{50}/2$, where d_{50} is the pore diameter, at which 50 % of the corrected mercury intrusion volume occurs, (Fig. 2). The derivation and validation of the d_{50} diameter is described in many previous publications and represents a well-accepted number based on the observed distribution function of our pore features. These show in the specific cases here that intrusion volume as a function of pore-size is a linear function of applied intrusion pressure with similar gradients between samples (Fig. 2). Since these functions are of the same form we can ignore parameters of the breadth of pore size distribution and use only a single parameter, d_{50}, to describe them. If a volume other than the 50 % filling would have been chosen, the resulting $d_{y\,\%}$ value would be only slightly shifted in either direction and not change the interdependent findings reported later.

LIQUID IMBIBITION METHODOLOGY

The recording of the position of the liquid front within the sample by eye or camera is imprecise due to the fuzzy appearance of the wetting front. This is assumed to be due to the previously discussed suspected preferred pathway flow at the liquid front. Therefore, the rate of liquid mass uptake was measured instead using an automated microbalance, namely a PC-linked Mettler Toledo AT460 balance with a precision of 0.1mg, capable of 2.7 measurements per second. A software program was developed [8] and improved further in the present work, interfacing with the balance for data sampling[6]. To provide a sufficiently slow and precise approach of the sample down to the liquid surface, a special sample holder was constructed (Fig. 3), - details of which are given elsewhere [8]. All experimentation in this study was maintained under constant temperature conditions of $23.0 \pm 1.5°C$.

As previously defined [8], the total force F_{total} acting on the solid-liquid interface during the imbibition of oil into the calcium carbonate network structure is the sum of the wetting, gravity and buoyancy forces, all of which are functions of time, t :

$$F_{\text{total}}(t) = F_{\text{wetting}}(t) + F_{\text{gravity}}(t) + F_{\text{bouyancy}}(t) \qquad (2)$$

Preliminary trials showed that the silicone ring around the basal edge is efficient in preventing fluid from creeping up the outside of the sample, so that, to a good approximation, $F_{side} = 0$. $F_{contact}$, (see Eq. 3), caused by the force of attraction around the perimeter of the meniscus pulling the liquid up towards the fixed solid, is constant for $t > t_1$, which, in the case of the viscous ink, can be significant. F_{base} is caused by the formation of the meniscus and the subsequent movement of fluid through the meniscus; the first effect is completed also in time t_1, and the second is assumed negligible because the meniscus is thin and the curvature slight compared with the total cross-sectional area of uptake. There is also inertia in the system which causes a lag and then an overshoot in the recorded weight. This effect is assumed to be completed in a time t_2, which is greater than t_1. Thus, to a good approximation in our experimentation,

$$
\begin{aligned}
F_{total}(t > t_2) &= F_{wetting}(t > t_2) \\
&= F_{wi}(t > t_2) + F_{base}(t > t_2) + F_{contact}(t > t_2) + F_{side}(t > t_2) \\
&= F_{wi}(t > t_2) + c
\end{aligned}
\tag{3}
$$

The constant term c can be found by fitting the function $F_{total}(t > t_2)$ with a linear regression as a function of the square root of time, and extrapolating back to $t = 0$, at which point $F_{wi} = 0$. Then the constant term can be subtracted from F_{total}, and F_{wi}, the wicking force or internal wetting force, can be calculated at all times. In practice, the forces are measured as apparent changes in liquid weight. Experiments with five similar samples were shown to have a repeatability within ±0.96 % in imbibition mass at 1 000 s [8].

ANALYSIS OF ABSORPTION RATES

Uniquely, we investigate structures over a range of different porosities using two closely related skeletal size distributions forming a range of mean pore radii whilst maintaining the

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chemical and overall geometrical similarity of the samples. The task is to analyse whether Lucas-Washburn really applies for porous network structures with surface properties held constant. All parameters in the Lucas-Washburn equation are known in this experimentation as they have been determined using independent methods. This gives us the opportunity to analyse the network contribution to the apparent pore-radius as if it would satisfy the Lucas-Washburn equation and then to see if this correlates with observation.

We begin by defining an equivalent hydraulic radius, r_{ehc}, for an equivalent hydraulic capillary (*ehc*) which behaves in the same absorptive way as the structures, independently of any preconceived absorption theory, related to volume uptake rates. It is also possible to define an *ehc* based on apparent Darcy imbibition distances or observed liquid front position into the structures as a function of time. The two definitions are not in themselves totally compatible if for any reason the complete porosity of the sample is not being filled at a given time, t, behind the wetting front. In a previous paper [23], we used the definition based on Darcy length where a difference of a factor greater than 4 was found between the measured r_{50} and the derived r_{ehc} for similar compressed tablets to those used in this work.

To understand the subtle differences a network makes when comparing between the Darcy definition and that defined by volume, let the porous structure that is actually filling be described first as a simple bundle of capillaries. This is only for convenience to visualise the relation between structure capillaries and the *ehc* and assumes nothing of the mechanism of a network structure. The real distance of the wetting front, x, absorbing into this bundle of capillaries is a function of surface energy comparison between the fluid and the skeletal surface; defined by $\gamma_V \cos\theta$ where γ_V is the fluid surface tension between the meniscus and the vapour phase (air) and θ describes the contact angle between the advancing meniscus and

the solid phase. Defining $\boldsymbol{\eta}$ as the fluid viscosity and r_c as the individual capillary radius in the bundle, and t is the time, then

$$x = f(\boldsymbol{\gamma}_{\mathrm{LV}}\cos\boldsymbol{\theta}, \boldsymbol{\eta}, r_c, t) \qquad (4)$$

is an expression for the distance travelled in that capillary at time, t.

The volume, $V(t)$, of fluid absorbed per unit cross-sectional area, A, of the sample at a given time, t, is therefore equated between the capillary bundle and the *ehc*,

$$V(t)/A = \sum_{i=1}^{N} x_i(t)\boldsymbol{\pi} r_{ci}^2 = x(t)\boldsymbol{\pi} r_{ehc}^2 \qquad (5)$$

where N is the number of capillaries per unit area accessing the surface of the sample. The Darcy length, x_{Darcy}, is defined as

$$x_{\mathrm{Darcy}} = \frac{V(t)}{A\boldsymbol{\phi}} \qquad (6)$$

where $\boldsymbol{\phi}$ is the measured porosity of the sample.

Now, suppose all the capillaries have the same radius, the actual wetting front distance x in the bundle will be the same as in just one capillary. The value of x_{Darcy}, however, is dependent on the sum of the volumes having entered into each capillary, i.e. the number of capillaries and the porosity these represent. Clearly, the porosity of a single capillary per unit area is far less than that of a bundle of N capillaries per unit area, hence the correction using the measured porosity takes care of this in a case where all the porous structure is simultaneously being filled behind the wetting front. When we have a distribution of capillary radii, the Darcy length now represents the distance of the wetting front based on the geometric mean of the capillary radii.

Consider a complicated system of tortuous paths intertwined, but not interconnected, still giving the same measured porosity. Now again, Darcy length will not relate to the observed wetting front, i.e. how far the liquid has imbibed into a complex sample, but $x_{\text{Darcy}}/x_{\text{observed}}$ represents a tortuosity. Therefore, the concept of Darcy length should not be confused with the progress observed in imbibition into real network structures, as it represents the length that would be present if the sample were modelled by a bundled distribution of straight capillaries given by the function of the geometric mean of their radii. If we were to derive an *ehc* based on Darcy length, as defined by Lucas-Washburn, it would follow

$$r_{\text{ehcDarcy}} = \left(\frac{V(t)}{A\boldsymbol{f}}\right)^2 \frac{2\boldsymbol{h}}{\boldsymbol{g}_{\text{LV}} \cos \boldsymbol{q} \, t} = \left(\frac{\mathrm{d}(V(t)/A)}{\boldsymbol{f} \mathrm{d}\sqrt{t}}\right)^2 \frac{2\boldsymbol{h}}{\boldsymbol{g}_{\text{LV}} \cos \boldsymbol{q}} \qquad (7)$$

The most important drawback using an $r_{ehcDarcy}$, (which includes an assumed porosity term), is, therefore, that it pre-supposes the complete filling of the available structure from the super source up to the liquid front.

We now, therefore, return to defining an *ehc* based on experimental volume uptake. As we described above, the measurement from experiment is that of liquid mass uptake as a function of time into the porous compressed pigment tablets of defined porosities. The pigments we know have constant $\boldsymbol{g}_{\text{LV}}\cos\boldsymbol{q}$ and the fluid properties are the same in all experiments. The experimental parameters are therefore:

$$m(t) = V(t)\boldsymbol{r} \qquad (8)$$

where $m(t)$ is the mass uptake at time t, as defined by a volume $V(t)$ of fluid of density $\boldsymbol{r}$. We normalise to the cross-sectional area of the sample, A, such that our data become $V(t)/A$, the volume absorbed per unit cross-sectional area of the sample.

It is shown experimentally that the rate of volume uptake, as mentioned before, does indeed approximate to a $\sqrt{t}$ relationship, (Fig. 4). Therefore, as our interest is primarily in rates of uptake, we can express each curve as a linear relationship between $V(t)/A$ and $\sqrt{t}$, the gradient of which we can write as

$$\frac{\mathrm{d}(V(t)/A)}{\mathrm{d}\sqrt{t}} = \frac{\mathrm{d}((m(t)/A)/\boldsymbol{r})}{\mathrm{d}\sqrt{t}} \qquad (9)$$

and which can be obtained directly from the plotted data by a linear regression analysis.

Experimentally, we see that the gradient of uptake volume as a function of $\sqrt{t}$ follows a linear relationship with porosity and this describes typically the absorption dynamic of our samples, both coarse and fine, (Fig. 5).

Assuming firstly the universality of the Lucas-Washburn equation, the volume uptake per unit cross-sectional area of the sample should be expressed in terms of the basic interactional parameters between fluid and the solid surface making up the boundaries of the pores as

$$V_{\mathrm{LW}}(t)/A = \frac{1}{A}\boldsymbol{p}\,r_{ehc}^{2}\sqrt{\frac{r_{\mathrm{ehc}}\boldsymbol{g}_{\mathrm{LV}}\cos\boldsymbol{q}\,t}{2\boldsymbol{h}}} \qquad (10)$$

formed by balancing the Laplace pressure across a curved meniscus with the Poiseuille resistive laminar flow in the circular capillary, and letting the volume uptake per unit area equal the volume filled into our equivalent capillary which represents that unit area. This definition no longer relates directly to the porosity of the sample and the incompatibility with a Darcy *ehc*, discussed previously, becomes a natural consequence.

We derive from Eqn *10* the r_{ehc} for each structure by comparing the experimental uptake gradients with the assumed parameters of the Lucas-Washburn equation acting over unit area, such that

$$\frac{\mathrm{d}(V(t)/A)}{\mathrm{d}\sqrt{t}} = \frac{\boldsymbol{p}\, r_{ehc}^{2}}{A}\sqrt{\frac{r_{ehc}\boldsymbol{g}_{LV}\cos\boldsymbol{q}}{2\boldsymbol{h}}} \tag{11}$$

from which r_{ehc} can be isolated as

$$r_{ehc} = \sqrt[5]{\left(\frac{\mathrm{d}(V(t)/A)}{\mathrm{d}\sqrt{t}}\right)^{2}\left(\frac{A}{\boldsymbol{p}}\right)^{2}\frac{2\boldsymbol{h}}{\boldsymbol{g}_{LV}\cos\boldsymbol{q}}} = \sqrt[5]{\left(\frac{\mathrm{d}V(t)}{\mathrm{d}\sqrt{t}}\right)^{2}\frac{2\boldsymbol{h}}{\boldsymbol{p}^{2}\boldsymbol{g}_{LV}\cos\boldsymbol{q}}} \tag{12}$$

Comparing this volume based *ehc* value with the value we obtained for an *ehc* based on Darcy (Eq. *7*), we see that

$$r_{ehc}^{5} = r_{ehcDarcy}\left(\frac{A\boldsymbol{f}}{\boldsymbol{p}}\right)^{2} \tag{13}$$

If Lucas-Washburn does in fact fail in that there exists selective pore filling, then it is to be expected that the definition of an *ehc* will not have the same dependency between the two size distributions with the measured r_{50} as it did with the measured porosity. The measured r_{50} values for our structures do not in fact fall on the same trend between pigments as a function of porosity, (Fig. 6). If we compare the experimental observations with those according to Lucas-Washburn as functions of porosity, $\boldsymbol{f}_{Hg}$, and pore size, r_{50}, we see that r_{ehc} scales with porosity, (Fig. 7) but does not scale between the two pigments as a function of pore size (Fig. 8). Since the absorption dynamic was shown experimentally to be dependent solely on porosity, and since all the Lucas-Washburn constants have been kept constant in these experiments, we must assume that the Lucas-Washburn equation does not hold true for differing pore size distributions in a network structure and that some pore selectivity occurs.

There must, therefore, be another factor involved in the dynamic of absorption which cannot be accounted for simply by the Poiseuille resistance to the flow developed under a Laplace pressure. This factor differentiates between pores of different dimensions other than by simple viscous drag, such that pores at the fine end of the pore size distribution behave under a different dynamic from those at the coarse end of the pore size distribution. This dynamic we assume as a first approximation to be related to inertia as the fluid is accelerated at high rates into small pore sizes in the network structure.

CONCLUSIONS

We have conducted imbibition experiments into a range of structures with different measured porosity and pore size distributions while keeping all the other important parameters of surface chemistry and geometry of the skeletal material constant. This formed the basis to analyse the applicability of the Lucas-Washburn equation for porous structures.

Definitions of the equivalent hydraulic radii derived from volume uptake rates and from calculated Darcy-length rates have been discussed. The implications arising from the use of an imbibed volume-defined equivalent hydraulic radius, thus removing the arbitrary dependency on porosity, have been illustrated.

Results showed that the absorption dynamic, in the experimental samples under study, was dependent solely on porosity. Since all the Lucas-Washburn constants have been maintained in these experiments, the lack of correlation between the measured pore radius and that of the derived porosity-independent equivalent hydraulic radius (based on volume uptake), for two similar but different pore size distributions, strongly supports the proposal that the Lucas-

Washburn equation does not hold true for differing pore size distributions in a network structure. To account for the discrepancy, models such as those provided by the inclusion of inertia are considered to provide a better solution, in which the individual fluid accelerations occurring within size-differentiated elements of a network structure lead to a deviation from straightforward Poiseuille flow simultaneously into every pore, such that pore selectivity occurs rendering the scaling of Darcy length with intrusion-measured porosity irrelevant.

FIGURE CAPTIONS

Fig. 1   Particle size distributions of the coarse and fine $CaCO_3$ powders used for consolidation of porous tablets expressed as cumulative mass % less than an equivalent Stokesian diameter.

Fig. 2   Typical Hg-intrusion curve as a function of the Laplace pressure related pore diameter, with the determined d_{50} pore value

Fig. 3   Gravimetric wetting apparatus.

Fig. 4   Imbibition curves for increasing porosities (from bottom to top, same order as in legend) normalised to $[V(t=0)/A]=0$ to remove wetting jump. Data shown are for the coarse $CaCO_3$ series.

Fig. 5   Both structure series, differing in pore size distribution only show similar volume rate imbibition as a function of porosity.

Fig. 6   The measured r_{50}-radius as a function of porosity for structures made from the two different skeletal particle size distributions.

Fig. 7   Lucas-Washburn-derived (volume based) rehc as a function of porosity shows quite similar behaviour for the two structure series, each differing in pore size distribution.

Fig. 8   Lucas-Washburn-derived (volume based) r_{ehc} as a function of r_{50}. Note that there is no direct scaling.
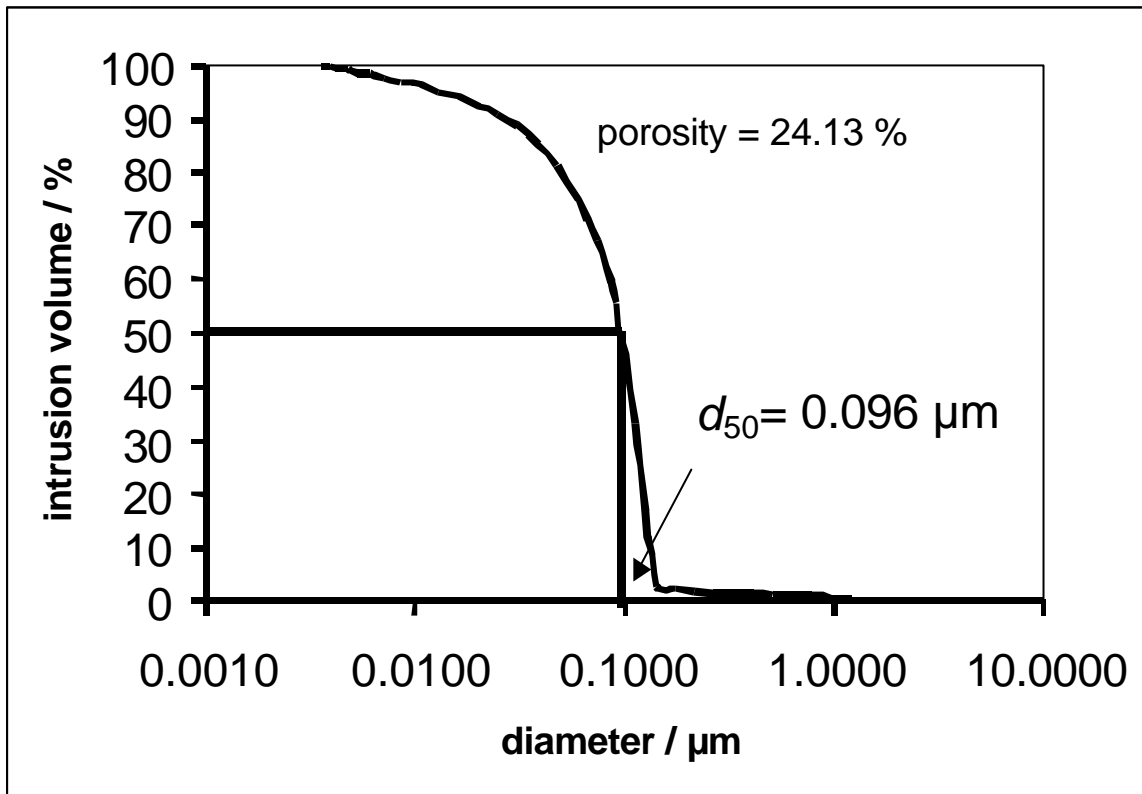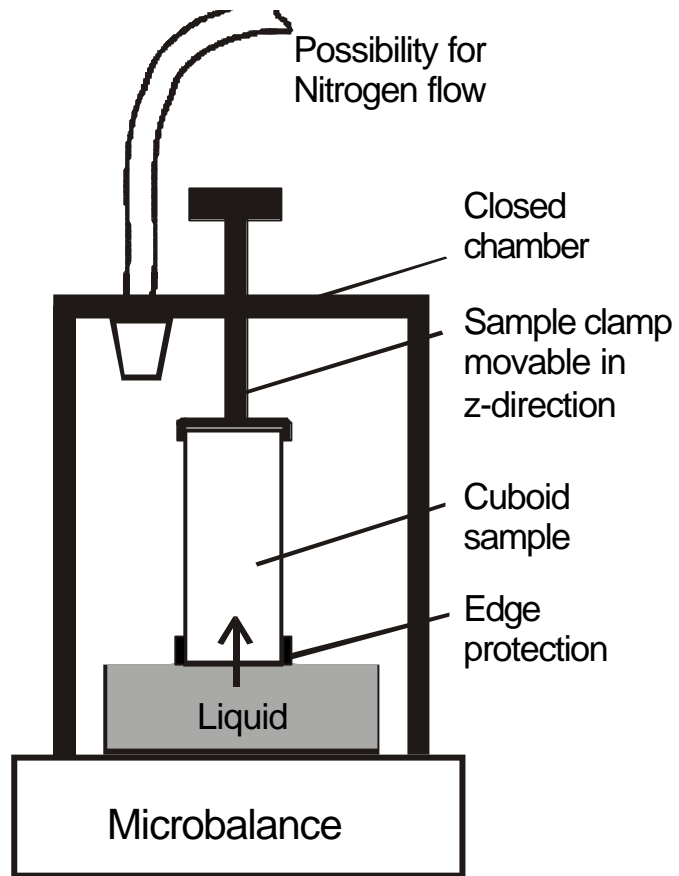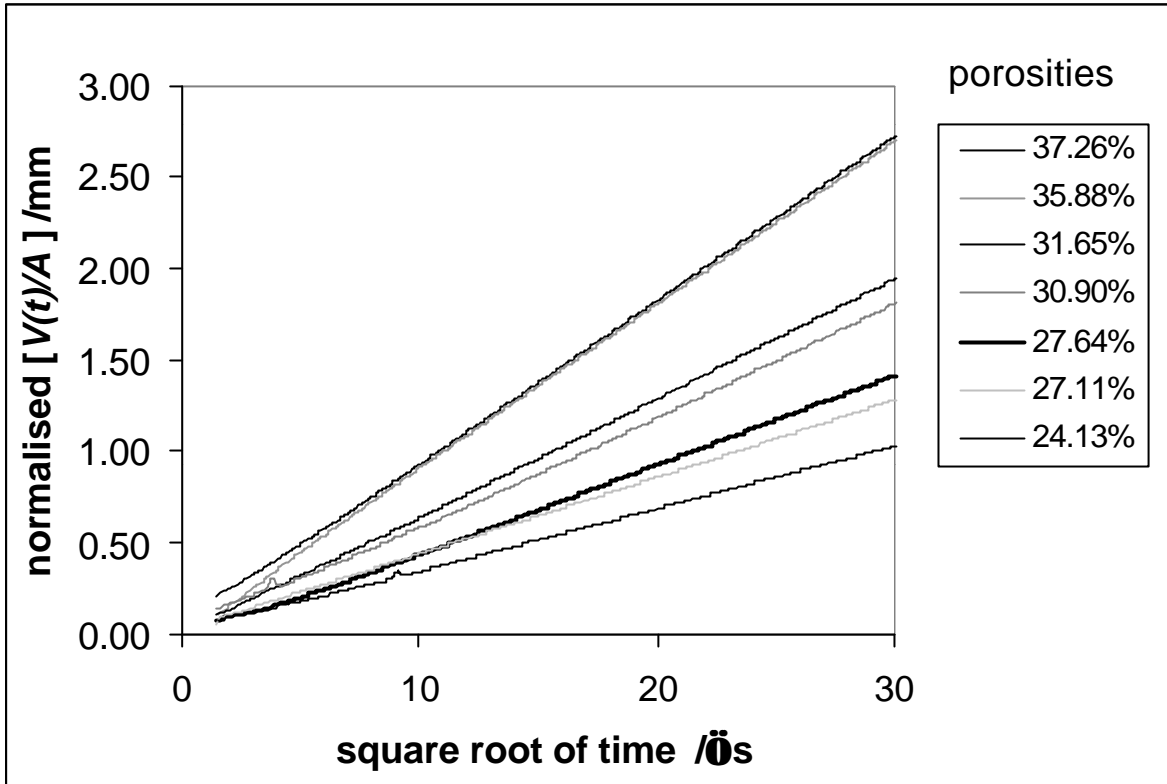
Fig. 1

Fig. 2.

Possibility for Nitrogen flow

Closed chamber

Sample clamp movable in z-direction

Cuboid sample

Edge protection
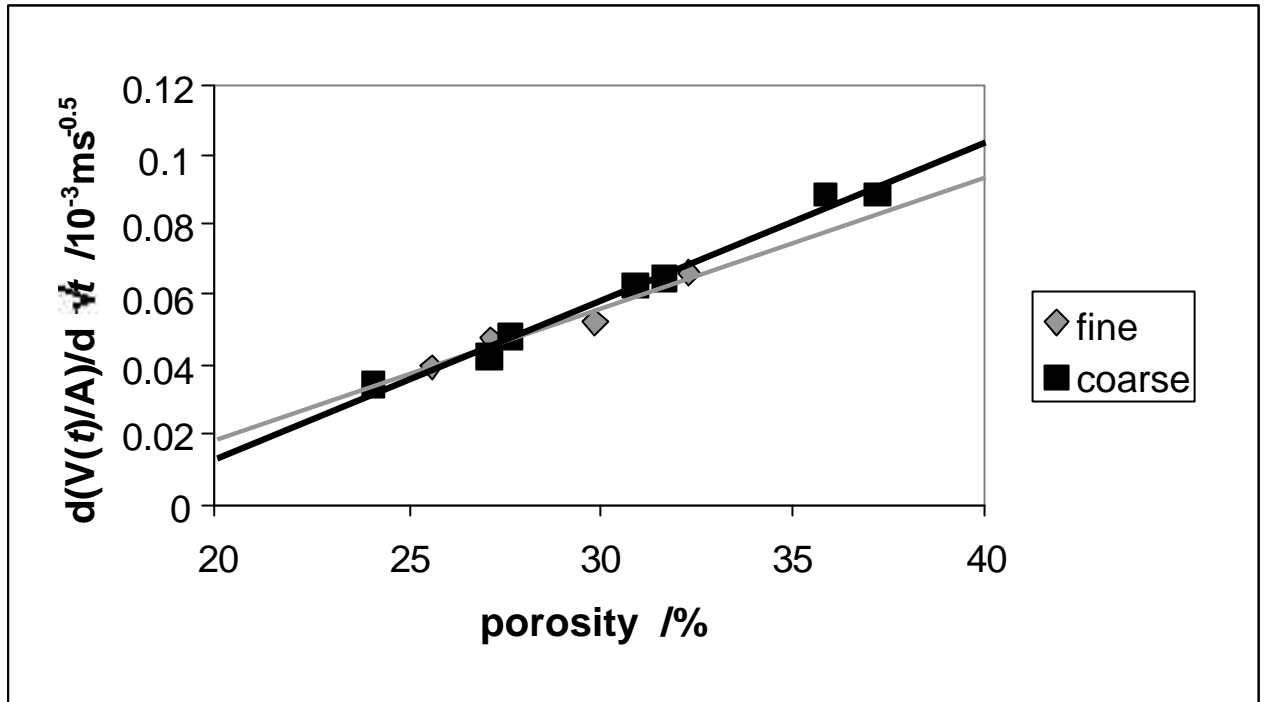
Liquid

Microbalance
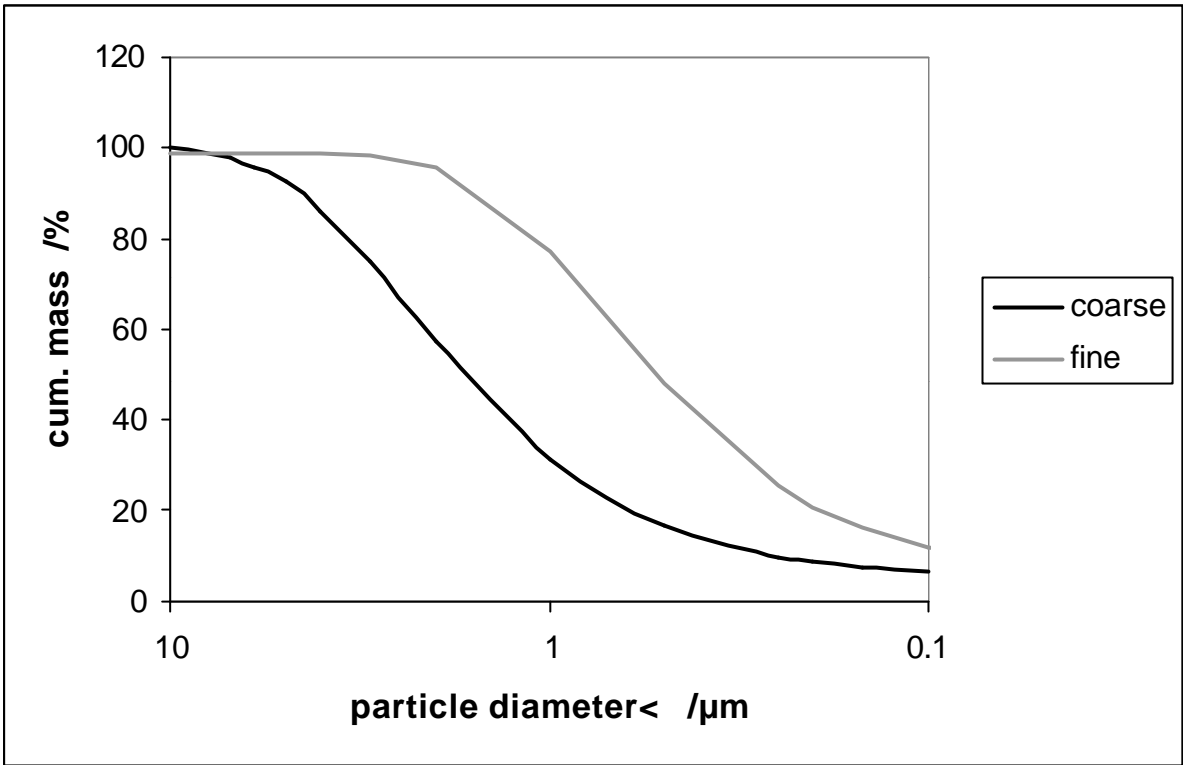
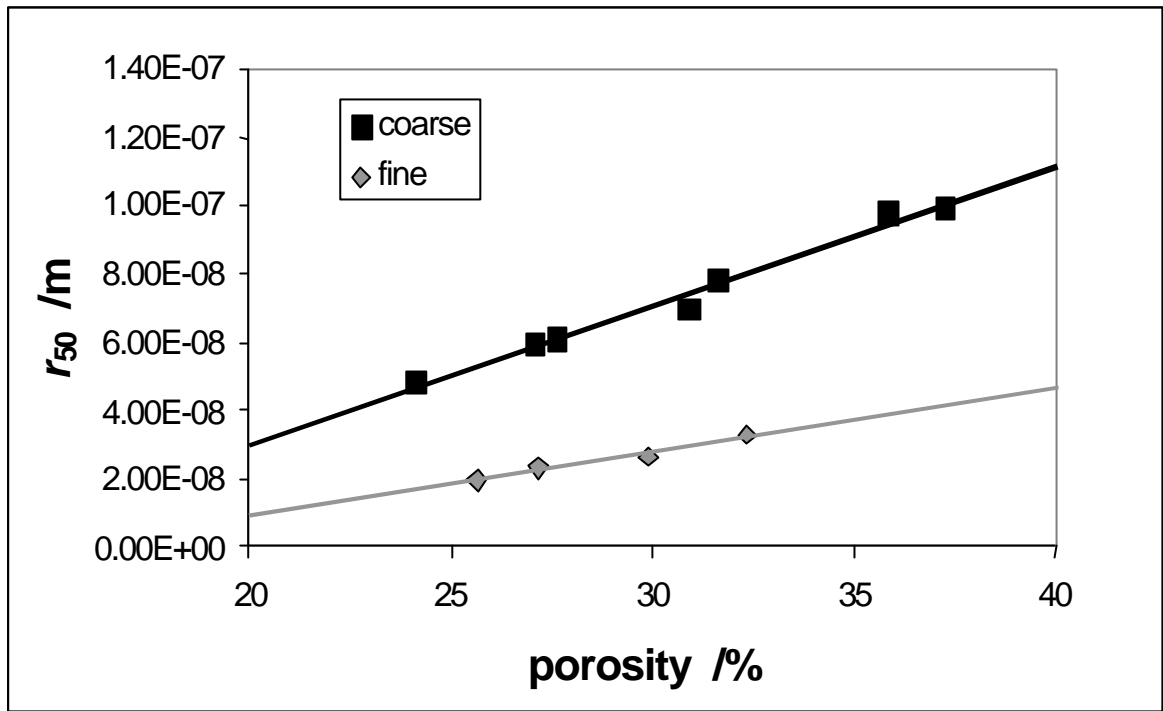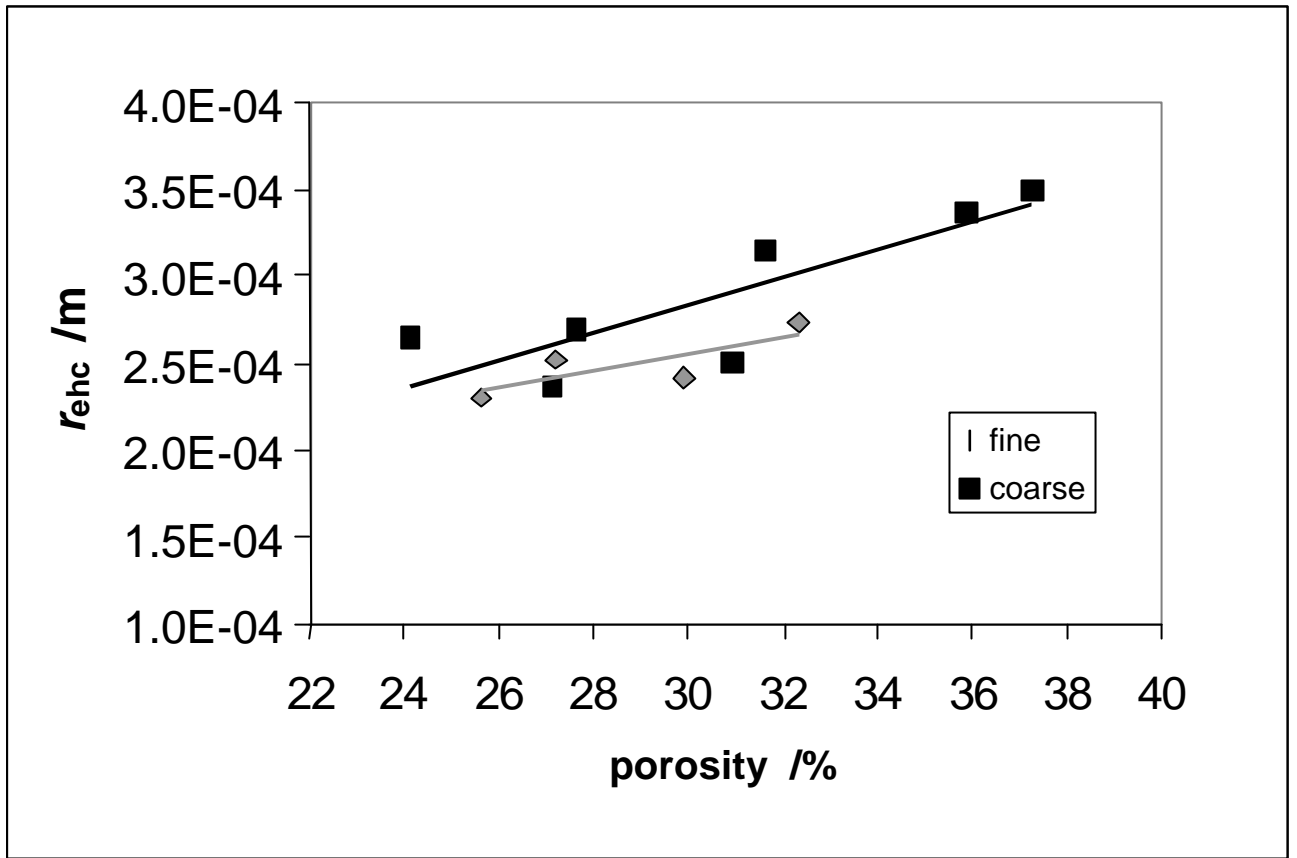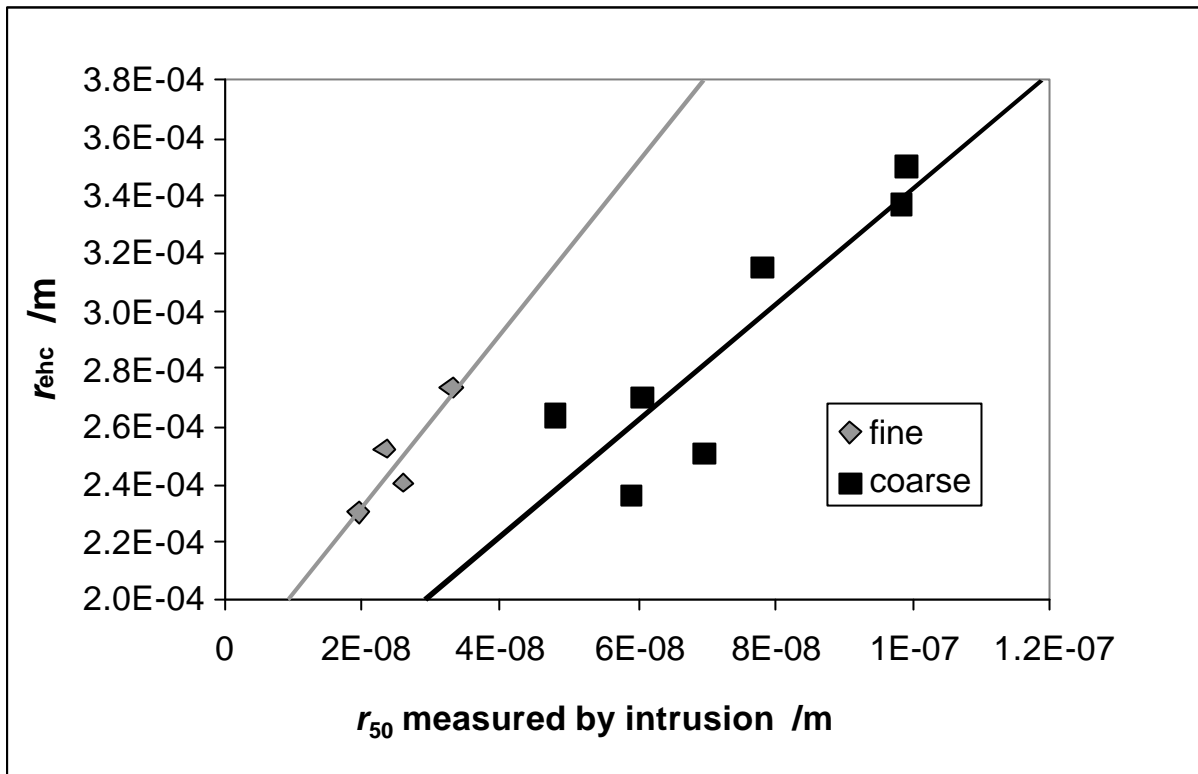*Fig. 3*

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

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