

Fluid Transport in Compacted Porous Talc Blocks

Viveca Wallqvist¹, Per M. Claesson², Agne Swerin¹, Patrick A. C. Gane^{3,4}
Cathy Ridgway³ and Joachim Schoelkopf³
(Communicated by Gustav Amberg)

Abstract: It has been shown that talc powder can be compacted into tablets with a preferred orientation of the platelets. The tablets can be obtained with different controlled porosity depending on pressing methods and applied pressure. The tablets can be obtained with or without additives, which may, in turn, be adsorbed. The orientation of the high aspect ratio platy talc, the surface chemistry imparted by the additives and the transported fluid influence the imbibition and permeation rates. Non-polar hexadecane displays a higher imbibition and permeability than water for all particulate orientations during short timescale absorption, likely due to the oleophilic nature of talc, and thus a more complete filling of the pores for non-polar liquids is to be expected. At longer timescales water is imbibed either at a similar rate to hexadecane or faster depending on the surface chemistry generated by additives leading to hydrophilicity. The swelling of the added polymers used to create wettability leads to break-up of the structure and exposure of hydrophilic surfaces for more rapid imbibition. It is not possible, therefore, to measure reliably the water uptake parameters when talc is fully dispersed with surfactants. Furthermore, dispersing agents tend to contribute to the blocking of pores and throats in the swollen state, and so a limitation in total imbibed volume occurs. The permeability under pressure is also inhibited by additives, which supports the suggestion of partial blockage of the pores and throats.

When the individual talc crystal c axes, defining the perpendicular to the [001] planes, are oriented 90° to the primary average liquid flow direction, i.e. are oriented in a planar configuration to the flow, imbibition and permeation of wetting liquid are increased. This is assumed to be due to decreased tortuosity, provided the liquid is wetting in respect to the oriented edge surface. However, non-wetting liquids in respect to all, or geometrically dependent, orientations are subject also to the surface chemistry presented by the orientation, i.e. whether the talc is primarily displaying OH-groups or not, or adsorbed species aiding wetting by the liquid. Measurements where additives are not strongly adsorbed are complicated by the solubility of some wetting and dispersing agents.

Keyword: talc, porous media, imbibition, surface chemistry, absorption, permeability.

1 Introduction

Talc is a naturally occurring mineral with the chemical formula $Mg_3Si_4O_{10}(OH)_2$. Pure talc mineral has hydrophobic properties due to its preferred breaking along laminar planes [Fig. 1], which exposes the non-polar and essentially inert basal plane. However, since the transplanar edges contain exposed OH groups, the measured hydrophobicity of pure talc is normally varying depending on particle size, grinding/breaking method and exposure time to air after cleavage. Talc is also known to contain impurities of other minerals, giving it a wide range of colours in addition to the white colour of pure talc. Water contact angles of 66-90° (for example see Michot, Villiéras, Franéois, Yvon, Le Dred and Cases (1994),

¹ YKI, Ytkemiska Institutet AB/Institute for Surface Chemistry, Stockholm, Sweden

² Department of Chemistry, Surface chemistry, Royal Institute of Technology, Stockholm, Sweden

³ Omya Development AG, Research and Technology Services, Oftringen, Switzerland

⁴ Helsinki University of Technology, Laboratory of Paper and Printing Technology, TKK, Finland

Yildirim (2001)) have been mentioned in the literature, the wide span quoted being due to the above mentioned differences between talc samples. Talc is used widely in the cosmetic, plastics and paper industries, in the latter mainly as filler and for the control of pitch and stickies, but also as a coating pigment.

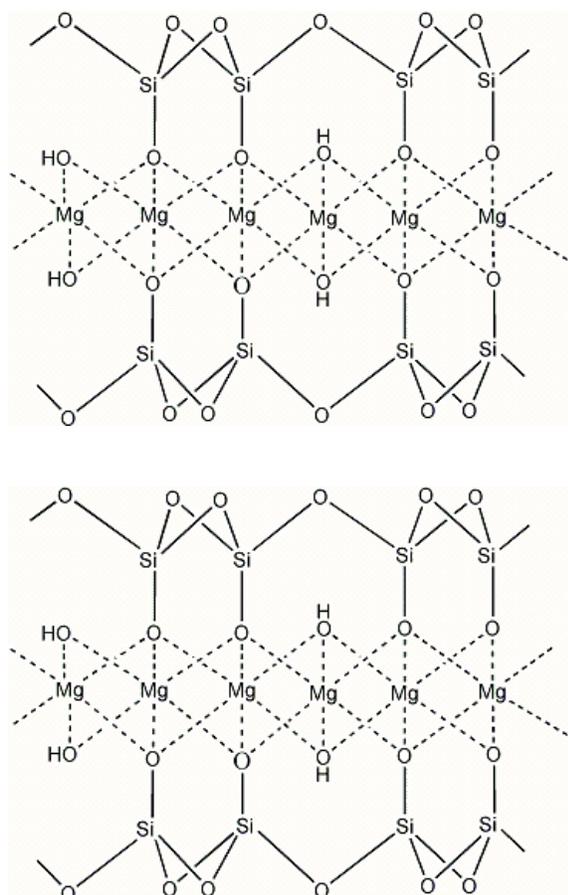


Figure 1: Talc structure

The platy structure of talc originates from the planar arrangement of the crystal habit, the planes being held together by weak van der Waals forces. As a result, ground talc consists of anisometric platelets [Fig. 2]. The platyness and hydrophobicity of talc combine to affect the properties exhibited when liquids contact the surface during imbibition throughout the porous structure created when talc platelets are packed together. Knowledge of these effects is relevant for paper properties, such as ink penetration and paper sizing, but also for other talc applications, such as in tablets

and cosmetics.

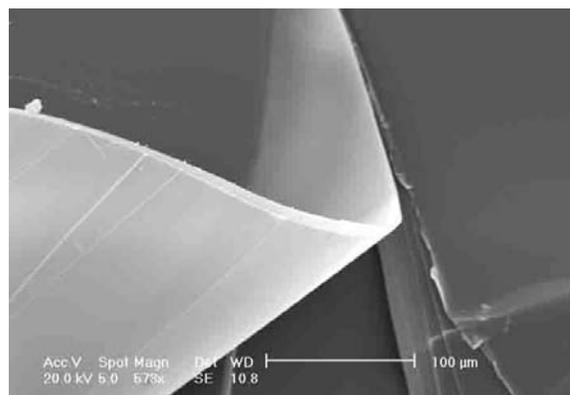


Figure 2: Scanning electron microscope image of a talc platelet structure

In this study the imbibition, permeation and porosity of compacted talc tablets have been measured. Such methods mimic on a measurable scale the structures encountered in paper coatings, following the work of Schoelkopf, Gane, Ridgway and Matthews (2002), in which calcium carbonate was the previous focus of analysis. Influences of tablet pressing method, added dispersing chemicals, interacting fluid polarity and its planar/transplanar interaction with oriented talc samples have been considered.

2 Experimental

2.1 Materials

Commercial talc P05 from Mondo Minerals (Omya AG) was used in all tests. XRD analysis using a Bruker AXS D8 Advanced XRD system showed it to contain the minerals talc, chlorite and magnesite, which was confirmed also by FTIR (using a Perkin Elmer Spectrum One Spectrometer) analysis. XRF (using a ARL 9400 Sequential XRF) gave a talc content of ~ 94 %.

Generic wetting and dispersing agents were obtained from Omya AG. The wetting agent consisted of a poly(ethylene oxide)-poly(propylene oxide) triblock copolymer with a MW of 2500 g/mol. The dispersing agent consisted of a standard sodium polyacrylate with a MW of 4000 g/mol.

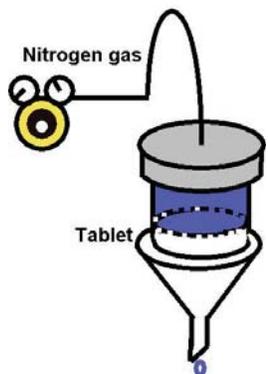


Figure 3: Wet press for tablet making of mineral powders

2.2 Methods

2.2.1 Compacted block preparation

Talc was used in two forms, either as provided, i.e. alone without additional chemical treatment (defined as “undispersed”), or with added wetting (1.1 wt%) and dispersing agents (0.2 wt%) (defined here as “dispersed”). Two tablet consolidation methods have been used; wet pressing and dry pressing. In the wet pressing method, suspensions of talc were pressure filtered in an aluminium cell (Fig. 3) using an over pressure of 25 bar. The resulting block was dried overnight in an oven at 60°C. The wet pressed tablets had a diameter of 4 cm and a height of approximately 3 cm. The tablets made by the dry pressing method were prepared by applying a force of 500 kN, equivalent to a pressure of 23.5 MPa, to the powder contained in a stainless steel cell (Fig 4). For the dry pressed tablets made from untreated P05 the powder was sprayed with a very small amount of water before the consolidation to aid compaction and integrity of the final tablet. Prior to the formation of dry pressed tablets made from P05 with dispersing and wetting agents, a slurry of the pre-mixed components was dried overnight in an oven at 60°C, thereafter it was ground to a powder. This powder was then consolidated in the dry press as previously described. The dry pressed tablets had a diameter of 4.5 cm and a height of approximately 3 cm.

A part of each sample was studied by mercury

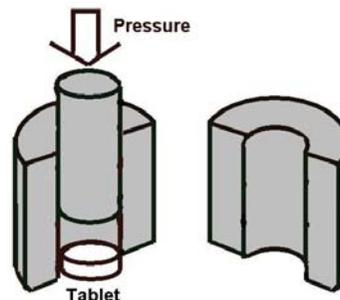


Figure 4: Dry press for tablet making of mineral powders

porosimetry, the remainder being cut and ground to form blocks of approximately 1 cm³ using a rotary disc grinder, which were then used for the liquid interaction experiments.

2.2.2 XRD and platelet orientation

In order to investigate the orientation properties of the samples in respect to liquid imbibition and permeation, the particulate orientation in the ground blocks was analysed by X-ray diffraction (XRD) from two orthogonal directions using a Bruker AXS D8 Advanced XRD system. This method was used to confirm the expected orientation of the platelets, i.e. with their planes parallel to the wet filter plane and orthogonal to the pressing direction, respectively.

2.2.3 Porosimetry

Laplace-defined pore diameters, naturally including pore shielding, and pore volumes of the consolidated talc blocks were determined using mercury porosimetry (Micromeritics Autopore IV porosimeter) and corrected for pressure chamber expansion, thermal expansion of mercury, compression of mercury and the compression of the talc skeletal material using the method described by Gane, Kettle, Matthews and Ridgway (1996), and adopted in the software Pore-Comp©. The maximum applied pressure of mercury was 414 MPa.

2.2.4 Contact angles

In order to obtain a rough estimation of the surface chemistry properties of the samples, contact

angles for the chosen liquids applied to the tablets were measured using a dynamic contact angle and absorption tester (FibroDAT 1100, FibroSystems AB, Sweden). Once again, orientation of the platelets exposed to the liquid was noted.

2.2.5 Imbibition

Imbibition was measured following the method of wicking as described by Schoelkopf, Gane, Ridgway and Matthews (2002). In order to reduce artefacts caused by external wetting of the outer surfaces of the formed tablets during imbibition, a thin barrier of silicone (Dow Corning 1-2577 low VOC conformal coating©) was applied around the base of the vertical edges of the cubic block. The remaining edges were not covered in order to allow the escape of air during liquid uptake and to minimise the interaction between the silicone wax and the liquid.

The imbibed weight of liquid was measured with an automated microbalance (Mettler Toledo AT 460) capable of 10 measurements per second (Fig. 5). The cubic sample with known dimensions was clamped in a special sample holder and slowly brought into contact with the liquid (water or hexadecane in this study), held in a reservoir acting as a supersource placed on the balance, i.e. the absorbed volume was measured as the mass loss, corrected for density, from the balance over time. For water, evaporation from the reservoir was taken into account by first measuring the water loss without any sample present and fitting the obtained values to a curve accounting for humidity build-up etc. This curve was then subtracted from the resulting absorption curves. No correction was necessary for hexadecane due to its low vapour pressure.

2.2.6 Permeability

For the permeation measurements, the cubic blocks were first embedded in a resin. The embedding was performed by placing the consolidated talc block with known dimensions in a PTFE mould (Prüfmaschinen AG, Switzerland) with an inner diameter of 3 cm and applying resin (Technovit 4000, Hereaus Kulzer, Germany) around it. When the resin was hardened, the edges

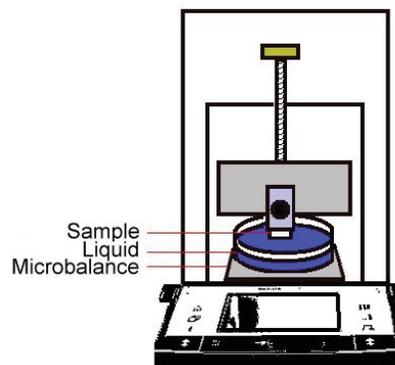


Figure 5: Absorption unit

of the sample were smoothed using a rotary disc grinder. The sample was allowed to saturate to the point of no further liquid imbibition using the chosen permeation liquid (hexadecane or water) before permeability was measured.

The permeation apparatus consisted of an aluminium cell filled with the permeating liquid on top of the sample (Fig. 6). The cell was placed over the same automated microbalance, described above, used in the imbibition experiment. An overpressure of 7 bar was applied to the cell, and the permeation was measured as the mass increase on the balance over time. For the water permeation measurements there was already water in the bowl on the balance at the start of the measurement and evaporation was further taken into account as described above.

3 Results and discussion

3.1 Compacted block preparation

The dry press consolidation produced well-formed stable tablets for both dry P05 (undispersed) and P05 with wetting and dispersing agents (dispersed). The wet press consolidation gave similarly stable tablets for dispersed P05, but for pure undispersed P05 the tablets retained a brittle nature, and could not be effectively ground into the desired shape. According to the work of Wallqvist, Claesson, Swerin, Schoelkopf and Gane (2006), in which atomic force microscopy was used to determine the spatial extent of the hydrophobic force when expe-

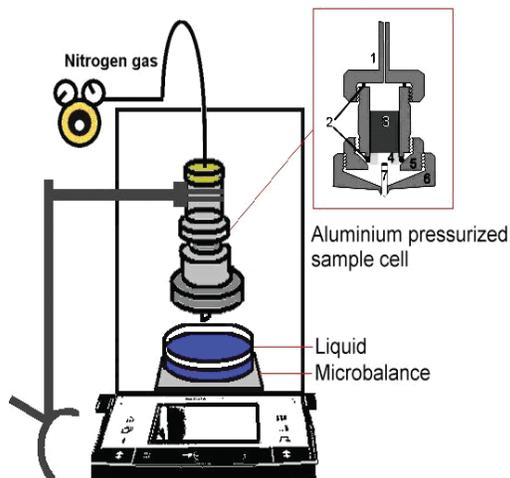


Figure 6: Permeation unit. Cross-section of the aluminium cell identifying the different parts as 1) lid with pressure inlet, 2) sealing O-rings, 3) liquid cell with outer diameter 4 cm, 4) talc sample embedded in resin disc of diameter 3 cm, 5) fixing ring compressing the O-ring which seals the resin disc, 6) security shroud and drop collector, 7) drop captor (teflon tube)

rienced by an oleophilic surface approaching and retreating from that of talc in water, it can be assumed that the formation of water-air menisci can be proposed. This finding provides some initial evidence for the action of adsorbed air within the confines of surrounding water, as might well be found in a suspension of undispersed talc. This effect is related to the surface tension characteristics of the water-air interface upon approach of the talc platelets to each other in the wet compression environment, such that the air layers may coalesce to form elastic entrapped volume between the talc platelets, which in turn act to expel water from the interface and so prevent an intimate contact zone. The resulting lack of platelet contact results in an inability to withstand mechanical forces and so the loss of integrity of the tablet during machining/grinding.

3.2 Orientation

It has been earlier demonstrated that pigment orientation can be investigated by X-ray diffraction, see Gane, Hooper and Grunwald (1995). The ori-

entation of the talc flakes within the tablets could be defined as the ratio of the intensity of the peaks [001] and [020]. When this ratio was compared across two different directions of the tablet, the orientation effects could be seen, despite the fact that the [020] peak was disturbed by the [110] and [-110] peaks. Tab. 1 displays the obtained values. It can be seen that there is a clear difference in the diffraction peak ratio depending on tablet orientation.

Table 1: Peak height ratio [001]/[020] for X-ray diffraction spectra taken from two directions of pressed talc blocks

	Top	Side
Undispersed, dry pressed	8.40	1.08
Dispersed, dry pressed	33.25	0.15
Dispersed, wet pressed	1.96	0.67

The peak ratios indicate that the platy structure of talc resulted in blocks having a layered structure with the plates oriented with the [001] planes facing the pressure direction. This allowed comparisons between imbibition and permeation studies of samples where the [001] plane was facing the liquid front (transplanar) or by using samples oriented 90° to this direction (planar). The wet pressed samples, although showing some ordering were seen to be somewhat more disoriented than the dry pressed samples. This is probably related to the reduced wet pressure and the necessary flow of liquid out of the sample during preparation, thus creating a favoured path of reduced resistance.

The orientation presentation to liquid flow was therefore defined as *trans* when the *c* crystal axis, perpendicular to the platelet planes, was parallel to the flow, and *planar* when the *c* axis was orthogonal to the liquid flow, as shown schematically in Fig. 7.

3.3 Porosimetry

The porosity, ϕ , fully corrected for compressibility was found to be 50 % for the wet pressed dispersed talc tablets, 22 % for the dry pressed undispersed talc tablets and 19 % for the dry pressed

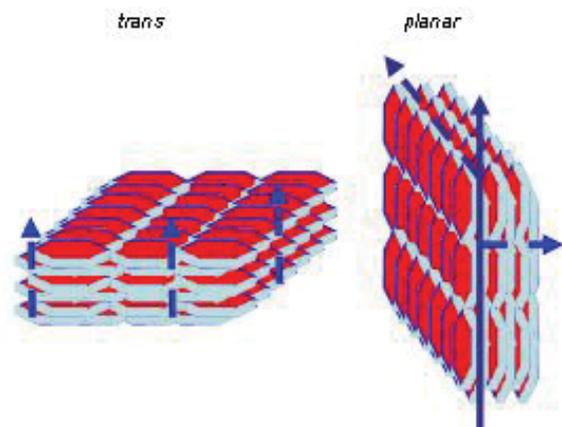


Figure 7: Orientation of talc platelets in the trans and planar configurations, respectively, showing the hydrophilic edges and oleophilic platelet faces

dispersed talc tablets. The difference between the dry and wet pressing methods is primarily due to the lower consolidation pressure employed in the wet press, i.e. that applied by the permeating water expressed by the gas overpressure. The difference between the undispersed and the dispersed talc tablets is assumed to be due to two main factors, firstly, and predominantly, the tighter packing derived from well-dispersed particles in water, as was the case in the pre-dispersing in water of the dispersed talc prior to drying, and, secondly, the potential for the additives to block some pores, each effect leading to a lower porosity. The pore blocking effect is expected to become more dominant when water is later used as the interacting liquid due to water layer adsorption and swelling of the wetting and dispersing agents.

In Fig. 8, the pore volume as a function of Laplace-derived pore diameter is displayed for the different samples. It can be seen that the pore sizes of the dry pressed undispersed talc and the dry pressed dispersed talc are approximately the same, but that the volume of the pores is marginally less in presence of additives. It can be concluded, therefore, that the pore distribution with and without additives is similar when intruded by mercury. Effects of breakthrough of the mercury into pores, otherwise blocked at their entry points by the polymers, cannot, however, be determined. For the dry pressed samples the

mean pore size is about $0.05 \mu\text{m}$, but a range of pore sizes between 0.1 and $2 \mu\text{m}$ is also present. This suggests the presence of regions where the platelets are perhaps stacked irregularly, resulting in crack-like voids in addition to the finer pore structure. The wet pressed dispersed sample contains significantly larger pores, the peak in the distribution is at the pore size of $0.45 \mu\text{m}$, and a greater associated pore volume than the dry pressed ones, as illustrated in Fig. 8. The details are summarised in Tab. 2.

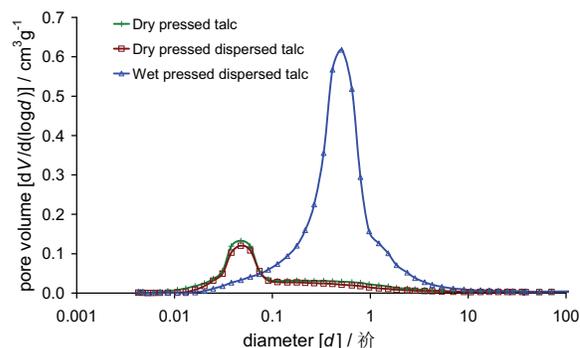


Figure 8: Pore volumes of dry pressed undispersed talc, dry pressed dispersed talc and wet pressed dispersed talc

Table 2: Pore structure summary of tablets

	Dry pressed	Wet pressed
Porosity / %	20	50
Average pore diameter / μm	0.05	0.45

3.4 Contact angles

Contact angles were measured by placing $4 \mu\text{l}$ droplets on the pressed tablets. The high-speed camera on the contact angle and absorption tester was able to take one image every 0.001 s . After having evaluated the images, the image 0.028 s after droplet-surface contact was chosen for the reported contact angle. At this time the oscillations of the droplet due to the droplet-surface impact had stopped and, in the case of water only, the imbibition into the structure had not yet had

a great effect on the droplet shape. In Tab. 3, the water contact angles for the various samples are reported. For hexadecane, no values could be reliably obtained since the imbibition began too soon and fast for a spherical droplet to form on the surface after impact.

Table 3: Water contact angles for pressed talc samples

Sample	Water contact angle °
Undispersed, dry pressed	75
(transplanar orientation at top face)	46
Dispersed, dry pressed	66

Surface wetting of powder samples is notoriously difficult to define due to factors such as inhomogeneous surface chemistry, surface microroughness, pore structure etc., though in the case of coarse pigments, especially when displaying orientated platelets, and hence greater surface continuity, the approximations used do carry some validity. It is noted, therefore, that the contact angle values give only a rough estimation of the surface chemistry properties of the samples, since the deviations from perfect surfaces are significant, for example they were increasingly inhomogeneous when rotated (edge face), and microrough – clearly indicated by the non-spherical nature of the droplets. For similar reasons the droplet method was abandoned for determining imbibition.

3.5 Permeation

The water permeation could not be measured for the dispersed talc samples containing wetting and dispersing agents. The reason for this was that the tablet slowly disintegrated in water, creating large holes in the tablet which prevented the pressure to be maintained.

The permeability, k , of a sample can be expressed using the following equation according to Darcy normalised for porosity, see Darcy (1856):

$$k = \frac{d(V(t)/A)}{dt} \frac{\eta l}{\Delta P} = \frac{q \eta l}{\Delta P} \quad (1)$$

where

k = permeability/m²

$V(t)$ = volume of liquid passing through the sample in time t /m³

η = viscosity of liquid/Pa s

A = sample cross-sectional area/m²

l = length of sample/m

ΔP = applied pressure difference/Pa

q = flux per unit area/ms⁻¹

The material can also be described by an equivalent tubular radius, r_{m^2} , through which the same flux would flow under Poiseuille conditions as would flow perpendicularly through one square metre of the sample, given by:

$$r_{m^2} = \left(\frac{8Q_{m^2}\eta l}{\pi\Delta P} \right)^{0.25} \quad (2)$$

where

Q_{m^2} = normalised flux (across unit area)/m³s⁻¹

r_{m^2} = equivalent tubular radius/m

3.5.1 Effect of Liquid on Permeability

In Fig. 9 and Fig. 10 it can be seen that for the undispersed samples, hexadecane flows somewhat faster under pressure than water, and the equivalent flow radius is also greater for hexadecane. Since the sample is saturated with the liquid before the experiment, i.e. the liquid has entered all those pores that it can wet, the permeability is primarily affected by the pore structure that is filled with liquid, i.e. its pore size distribution and connectivity associated with liquid, since the viscosities of the two liquids are similar. It is likely, therefore, that the saturation step by pre-absorbing water is microscopically incomplete. This may be due to the existence of air pockets within the structure caused by the higher contact angle for water, leading to unfilled large pores that are entered only by small throats (imbibition terminating geometries), see Kent and Lyne (1989), and the potential of air coalescence under the action of the hydrophobic force when surrounded by the water-air interface menisci, see Wallqvist, Claesson, Swerin, Schoelkopf and Gane (2006). The difference is maintained also for the samples

oriented with the platelets parallel to the flow (i.e. in planar orientation).

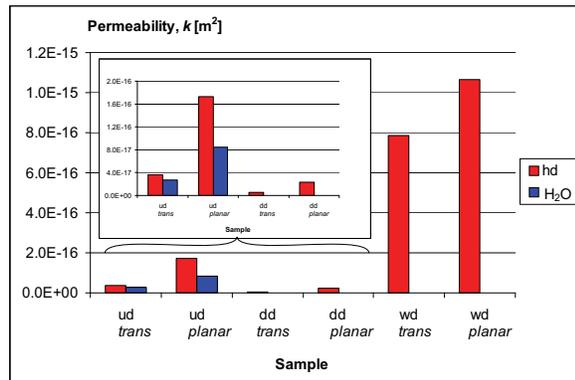


Figure 9: Permeability, k , for pressed talc samples. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane

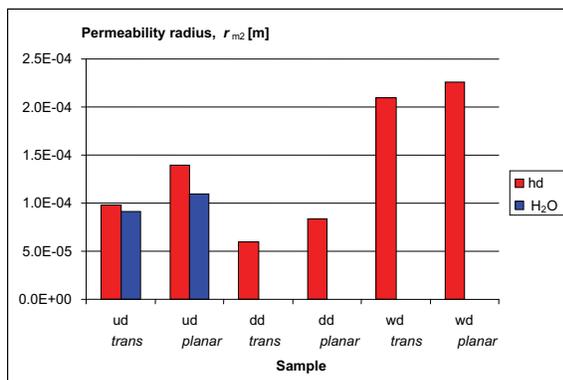


Figure 10: Equivalent Poiseuille permeability radius, r , for pressed talc samples. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane

Direct observation of the samples after exposure to liquid “saturation” readily supports the hypothesis of incomplete filling of the tablets by water. The photographs shown in Fig. 11 illustrate the lighter appearance of the water-imbibed sample, indicating clearly the presence of entrapped air at the mineral boundary leading to higher light scattering. The dark nature of the hexadecane-filled sample shows the complete filling of all available pores.



Figure 11: Photographs of the imbibition-filled samples showing on the left the lack of complete filling for the water exposed sample (lighter), related to the light scattering of entrapped air, versus on the right the more complete filling for hexadecane (darker)

3.5.2 Orientation of the talc in respect to liquid flow

Fig. 9 and Fig. 10 also display a higher permeability, and larger equivalent radius, for the samples in planar orientation than for samples having the [001] planes oriented perpendicular to the liquid flow direction (trans). One reason for this is that the parallel alignment of the platelets with the direction of flow reduces the tortuosity of the flow channels, where tortuosity is defined as the microscopic internal path length divided by the macro external dimension of the sample. This is further supported by the highly porous sample made from the wet pressing of dispersed talc, with its less ordered structure, in which the effect of sample orientation is greatly reduced. Since the sample is pre-saturated to the point allowed by wetting, the surface chemistry of the talc cannot play a role other than due to adsorbed layer formation, which would act to slow down permeation and not speed it up.

3.5.3 Wetting and dispersing agents

In Fig. 9 it can be seen that the wet pressed dispersed sample, containing wetting and dispersing agents, displays the highest permeability. Since, in Fig. 10, the equivalent radius follows the same trend, it can be concluded that surface chemistry is not affecting permeability, as would be expected since the structure is pre-saturated and no

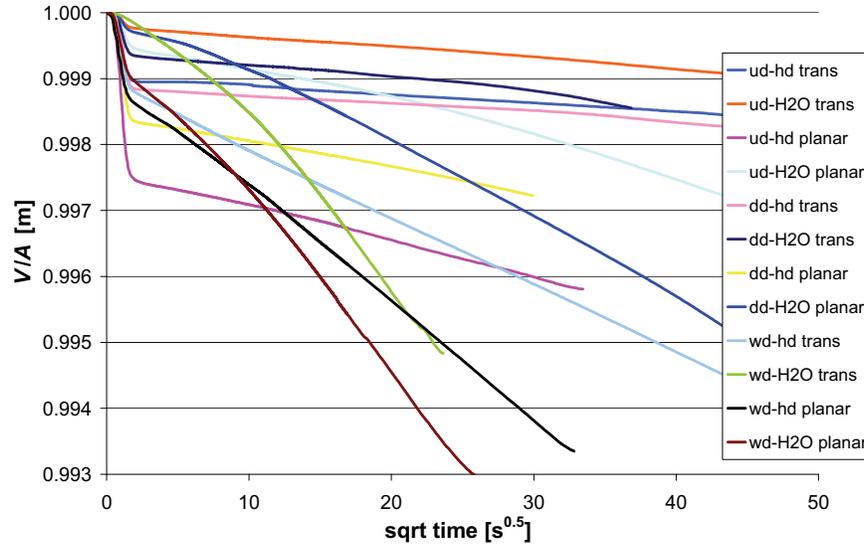


Figure 12: Imbibition into pressed talc samples for water and hexadecane. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane, H2O = water, trans = transplanar imbibition, planar = turned 90° for imbibition. The y axis is arbitrarily set to a starting point of 1, units are absolute and represent amount from this starting point absorbing into the sample

wetting fronts are supposed to exist. The only accepted effect of the polymers' presence would be a swelling in the presence of adsorbed water, and since permeability could not be measured due to this very effect, it cannot be quantified. Furthermore, as we saw, the porosity of the wet pressed sample is significantly greater than for the dry pressed samples, and so it is to be expected that permeability for similar structures will be greater.

3.6 Imbibition

Imbibition curves were plotted, after defining time, t , as the time after initial contact, as liquid volume/sample area exposed towards the liquid front against $t^{0.5}$. The imbibition curves consisted of two regions; the initial short-time absorption (approximately 0.7 - 1.8 s after contact) and the long-time uptake, which in this study was measured after 1 min. Examples of imbibition curves for all combinations of sample and liquid are displayed in Fig. 12. The imbibition speed, ξ , with respect to $t^{0.5}$, can be additionally expressed as a Darcy rate, reflected by the following expression:

$$\xi = \frac{\frac{d(V(t)/A)}{d(\sqrt{t})}}{\phi} \quad (3)$$

where

ξ = imbibition speed/m*s^{-0.5}

$V(t)$ = volume of liquid passing through the sample in time t/m^3

A = sample cross-sectional area/m²

Φ = sample porosity (as determined by mercury porosimetry)

This expression, represents the idealised distance that a straight, even wetting front would pass into the sample of given porosity ϕ after $t^{0.5}$. In practice, wetting fronts are not straight but distinctly uneven due to the preferred pathway dynamics, described amongst others by Schoelkopf, Gane and Ridgway (2004).

The water imbibition into the dispersed talc tablets containing wetting and dispersing agents was complicated by the fact that they slowly disintegrated in water, an effect similar to that seen above during the permeability tests, i.e. they self-dispersed in the water. Despite this disintegration, absorbed volume could be recorded, but the path length in the sample was proportionally reduced due to the dispersing action as a function of time, and this, together with the expansion of the sample pores during disintegration, is assumed

responsible for the deviation from the expected straight line relation with the square root of time for these samples shown in Fig. 12. The disintegration and delamination of the samples is illustrated in Fig. 13. Furthermore, in Fig. 12, it is also seen that undispersed samples in the planar configuration deviate somewhat from the straight line behaviour. This could be explained by the fact that edge pathways for water (the only hydrophilic pathway) can lead to two phenomena: (i) air entrapment which can then dissolve in water and so increase "apparent permeability with time" by permitting more complete filling of the pores and (ii) edge forces may well lead to rearrangement in the structure if the local compression force used to make the oriented tablets retained some clumping effect of particles due to the fact that the particles were not originally well dispersed.

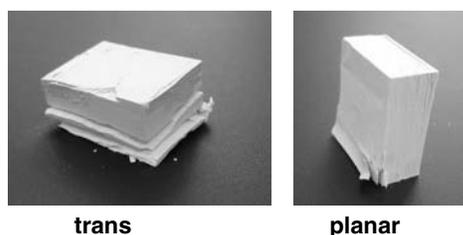


Figure 13: Photographs of the disintegration effect of water on dispersed talc samples showing the delamination and expansion of pore size

3.6.1 Short-time imbibition

Fig. 14 describes the short-time imbibition rates for the various talc samples. Fig. 15 describes the volume per unit area $V/A/\phi$ as a function of time (flux) during the short-time imbibition, i.e. the Darcy distance rate into the structure that the liquid travels during the short-time imbibition, ξ . Among factors that can be identified as influencing the short-time imbibition are; pore size, relative pore shape, presented surface chemistry, liquid properties and chemical additives properties. The short timescale imbibition assumes that Poiseuille flow is not fully established and so permeability plays only a secondary role.

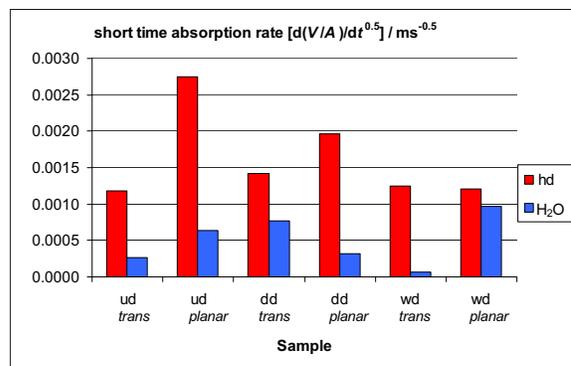


Figure 14: Short-time imbibition for pressed talc samples. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane, H₂O = water, trans = transplanar imbibition, planar = turned 90° for imbibition.

3.6.1.1 Liquid effect at short times It can be seen clearly that hexadecane has a faster short-time imbibition rate into the talc structures than water, even when wetting agents are present, though the planar absorption for water into dispersed talc when the porosity is high (wet pressed dispersed talc) is almost as fast. Clearly the surface chemistry plays a role in determining the wettability by the liquids. As mentioned earlier, this trend for lower contact angle for water on dispersed talc was also seen in the droplet contact angle.

It has earlier been noted in the literature that materials poorly wetted by water exhibit a water absorption rate of about four orders of magnitude slower than for lower surface tension liquids, see Clarke, Blake, Carruthers and Woodward (2002). One theory is that the transfer of liquid from smaller to larger pores is partly inhibited in the case of low wettability (imbibition terminating structures), resulting in an only partially filled pore structure. This is corroborated in the present study. It has also been shown that when non-adsorbing liquids are used, the imbibition rate is independent of the liquid, see Labajos-Broncano, Antequera-Barroso, González-Martín and Bruque (2006). This indicates that the faster imbibition of hexadecane is partly due to the higher affinity of hexadecane for the talc surface

and that adsorption can be proposed. Similar results were obtained in a comparison of hexadecane and water imbibition on the short timescale for calcium carbonate structures, see Ridgway and Gane (2003), where it was assumed that the finer pores governing the short timescale imbibition rate were effectively less polar in their expression of surface chemistry.

3.6.1.2 Orientation – surface chemistry and adsorbed polymers In Fig. 14 and Fig. 15 it is seen that in most cases the samples oriented in the planar direction are the faster imbibing on the short timescale, and clearly absorb the largest amount of liquid. This is also likely to be surface chemistry related as once again the energy loss terms described by permeability, i.e. tortuosity, have not yet been established under sufficient flow into the structure. It can be assumed that the more hydrophilic edges create a greater imbibition delay for both hexadecane, due to lack of wetting, and for water, due to the time constant of adsorption. Interestingly, the dry pressed dispersed sample shows the greater decreasing rate of water imbibition in comparison with that of hexadecane when the platelets are parallel to the flow direction. This may also be due to the likely swelling of the adsorbed polymers on the talc faces in the presence of water, this being particularly the case for the polyacrylate portion of the dispersing system, and since the packing in this sample is tight, the space for flow is restricted. This view is supported by the faster uptake of water into the more porous, more permeable, wet pressed dispersed sample.

Initial imbibition has been known to occur into interstices in the solid (Labajos-Broncano, Antequera-Barroso, González-Martín and Bruque (2006)) and since the layered material contains such interstices, or cracks, between the platelets, the orientation of these interstices toward the liquid flow may also play an enhancing role.

One should also note that the planar structures where the [001] planes are placed parallel to the liquid flow are more likely to have a larger number of pore and throat entries in contact with the

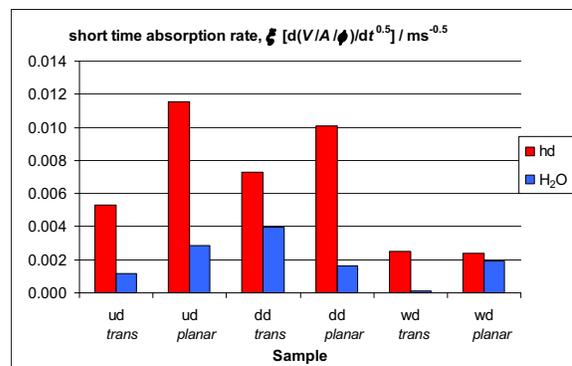


Figure 15: Rate of change of fluid front position in pressed talc samples during short-time imbibition. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane, H₂O = water, trans = transplanar imbibition, planar = turned 90° for imbibition

liquid.

3.6.1.4 Porosity It has been reported elsewhere that the short-time imbibition is related to the preferred filling of fine structures (Ridgway, Gane and Schoelkopf (2002)). In the porosimetry results it is observed that the dry pressed samples contain finer pores than the wet pressed samples. It is further noticed that the pore volume is lower for dry pressed samples. In Fig. 14 it can be seen that the wet pressed sample with the larger pores generally imbibe slower in the short timescale than the samples with smaller pores, thus confirming the important role of the finer pores in the short timescale imbibition rate. Furthermore, comparing Fig. 14 and Fig. 15 shows that when the platelets are oriented perpendicular to the liquid flow (trans), the wet pressed sample has a similar dynamic as the dry pressed sample with respect to hexadecane volume uptake, this despite the increased pore volume of the wet pressed material. This leads to the conclusion that within the short-time imbibition a larger percentage of the dry pressed tablets are filled with liquid than the larger pore size wet pressed tablets. The implications for permeability are now reinforced, in that retained air pockets are likely to occur, especially in the case of water, even though the material has

been allowed to reach “saturation” for the given liquid.

3.6.2 Long-time imbibition

Fig. 16 displays the long-time imbibition rate measured 1 min after liquid contact. The data for the longer timescale now include the role of permeability, as it can be assumed that Poiseuille flow is more likely to have been established. Structural effects are now acting as the limiting energy loss factor opposing the fine scale wetting force within the material.

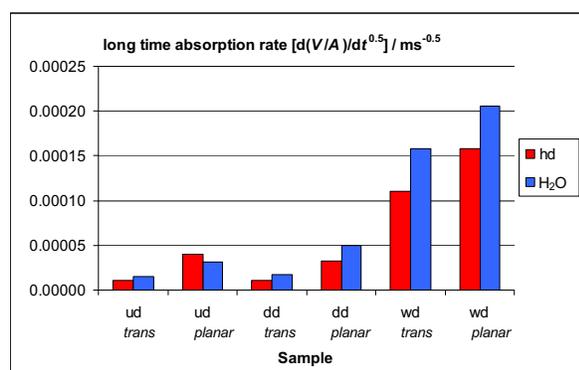


Figure 16: Long-time imbibition rate after 1 min for pressed talc samples. Abbreviations: ud= undispersed and dry pressed, dd = dry pressed and dispersed, wd = wet pressed and dispersed, hd = hexadecane, H₂O = water, trans = transplanar imbibition, planar = turned 90° for imbibition

3.6.2.1 Effect of liquid It can be seen that the long-time imbibition rate for water is now faster than for hexadecane. Thus, the difference between short-time and long-time imbibition rate for water is greater than for hexadecane. However, the implications are more far reaching if it could be shown that the surface chemistry is effectively different for the fine versus the larger pores, although the impact of swelling of polymer is likely to be one important factor. Nonetheless, for the undispersed material the same argument can be applied, i.e. the finer pores, most likely structurally to be related to the nodes where the particle edges come into contact, and thus the exposed OH groups have an important impact on

the comparative hydrophilicity of the edges versus the faces. The progress of water imbibition is then more likely to follow preferred edge contours compared with the hexadecane, which would follow the more general structure, and, considering the greater capillarity of the smaller edge and nodal features providing the wetting force, the progress of water might be related to the higher wetting forces experienced, despite there being less of the overall structure being filled. Finally, we must consider the partial disintegration and opening of the structure of the dispersed samples in the presence of water. It is proposed that the delamination of the structure may be related to the swelling of adsorbed polymer layers as they adsorb water. This leads to a structural disintegration of the tablet, increasing permeability and so increasing the volume uptake of water over the longer timescale.

3.6.2.2 Orientation The long-time imbibition rate is higher for the planar samples than for those having the [001] planes oriented perpendicular to the liquid (trans). Even though the structure might be close to saturated, slow redistribution of liquid drives the imbibition further. Since more “entrances” to the structure are available for the planar samples, this redistribution is facilitated for these samples.

These results fit with the assumption that the longer term imbibition is predominantly permeability controlled, and, as we saw in the case of permeation, the tortuosity developed by the platelets being perpendicular to the flow significantly increases the flow resistance towards the wetting front, and vice versa for the planar sample.

3.6.2.3 Wetting and dispersing agents The samples containing wetting and dispersing agents are also orientation dependent in their absorption properties, in that the dry pressed sample with strong orientation displays a greater long-time imbibition for the case where the platelets are parallel to the flow compared with the case where the platelets are perpendicular to the flow for both liquids, although the effect is stronger for water

(Fig. 16). Since water also acts to disintegrate the compacted tablets containing dispersing and wetting agents, this dissolution might after some time create more voids and thus faster long-time imbibition rate particularly in the planar orientation. Furthermore, the disintegration itself means that the permeability greatly increases as a function of time and so the resistance to flow diminishes. The additives are also facilitating the redistribution into pores hard to reach since they increase the adsorption and thus the wettability by water.

Interestingly, due to the increased permeability of the less oriented wet pressed sample, the long term imbibition difference between the two orientations is markedly less than for the more highly oriented samples. This confirms the primary role of tortuosity, and the fact that the less oriented sample has a less marked tortuosity difference. Once again it can be concluded that the long term imbibition is permeability controlled.

4 Concluding remarks

It has been shown that talc powder can be compacted into tablets with a preferred orientation of the platelets. The degree of orientation depends on the pressing method, with dry pressing giving greater orientation than simple pressure filtration of dispersed talc. The tablets can be obtained with different porosity depending on pressing methods and pressure. The tablets can be obtained with or without additives, assumed adsorbed on the surface, such as wetting and dispersing agents.

Imbibition and permeation of chosen liquids can be performed using the tablet structures. The orientation of the talc platelets, the presence or otherwise of additives and the nature of the transported fluid influence the imbibition and permeation rates, the latter mostly via the lack of saturation of the complete structure when polar liquid is used. When the [001] planes are oriented 90° (perpendicular) to the liquid, imbibition and permeation are decreased. Conversely, the greatest flow rates are obtained when the platelets are parallel to the flow both in the short timescale response and during longer timescale imbibition. This shows that the structural resistance to flow is dominant at long timescales, whereas the lo-

cal surface chemistry and its orientation to the liquid are dominant at short timescales, including the finer pore structure and its prevalence. This is visualised by the OH groups associated with edge sites, or the adsorbed wetting agent and dispersing species, together with the nodal effect of fine pores created by the arrangement of edges acting as the decisive pore surface chemistry differentiating character.

Non-polar hexadecane displays generally a faster imbibition and permeability than water on the short timescale, likely due to the increased affinity/wetting of hexadecane for the oleophilic talc surface, and thus a more complete filling of the pores for this liquid. Wetting and dispersing agents though increasing the imbibition of water by increasing the wettability also contributes to an assumed swelling and blocking of pores and throats by adsorption of water. This swelling is assumed responsible for the disintegration process observed for dispersed talc contacting water. Permeability under pressure is inhibited by tortuosity, and so is strongly related to platelet orientation. Permeability is seen as the major controlling factor, acting as a resistance term, in the long term imbibition properties.

Acknowledgement: Omya Development AG is thanked for funding this project and for supporting cooperation between its industrial Mineral and Surface Chemistry R&D.

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