

Advances in the fundamentals of fine coal filtration

Florent Bourgeois, Wesley Barton

▶ To cite this version:

Florent Bourgeois, Wesley Barton. Advances in the fundamentals of fine coal filtration. International Journal of Coal Preparation and Utilization, 1998, 19, pp.9-31. 10.1080/07349349808945571. hal-02136647

HAL Id: hal-02136647

https://hal.science/hal-02136647

Submitted on 22 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



OATAO is an open access repository that collects the work of Toulouse researchers and makes it freely available over the web where possible

This is an author's version published in: http://oatao.univ-toulouse.fr/3507

Official URL: http://dx.doi.org/ 10.1080/07349349808945571

To cite this version:

Bourgeois, Florent and Barton, Wesley *Advances in the fundamentals of fine coal filtration*. (1998) International Journal of Coal Preparation and Utilization, 19. 9-31.

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Advances in the Fundamentals of Fine Coal Filtration

F. S. BOURGEOIS^a and W. A. BARTON^b

Department of Mining, Minerals and Materials Engineering,
 The University of Queensland, Brisbane, QLD 4072, Australia;
 CSIRO Division of Coal and EnergyTechnology, PO Box 136,
 North Ryde, NSW 2113, Australia

The fundamental principles governing the filtration of fine (nominally -0.5 mm) coal are not well understood. This has recently been recognised by the Australian coal industry as a major hurdle to significantly improving dewatering technology and performance. This study quantifies and compares the respective influences of filter cake microstructure, and coal surface and bulk properties on the vacuum filtration of fine bituminous coal slurries. It is shown that filter cake microstructure is the dominant factor, particularly in determining the kinetics of cake formation and desaturation. Although variations in coal properties probably have little effect on the filtration kinetics, they can significantly influence residual cake moisture. Moreover, the results obtained in this study indicate that there does not exist a single microstructure capable of providing both a high filtration rate and a low product moisture. Such a result is expected to influence future dewatering research efforts and possibly drive the design of new fine coal filtration technologies.

Keywords: Coal; fine coal filtration; filter cake microstructure; coal properties

INTRODUCTION

The Australian coal industry is coming under increasing customer pressure to reduce product moisture. High product moisture is undesirable for economic and technical reasons, such as increased transport costs, handling problems and reduction of efficiency with which coking and thermal coals can be used. In recent years, coal

beneficiation plants have made considerable efforts to increase their production rate and deliver a cleaner product. One major hurdle to the realisation of the benefits of these efforts is the overall inefficiency of the fine coal dewatering process. Furthermore, vacuum filters, originally designed to handle coarser slurries, are showing limitations when handling the large amounts of incoming fine and ultra-fine particles recovered by newer and better performing flotation technology. Presently, typical fine coal dewatering circuits produce filter cakes with moisture contents of the order of 20 to 25 percent, which often are sufficiently high to prevent coal preparation plants from achieving an overall product moisture that meets increasingly stringent customer specifications.

The lack of understanding of the fundamental principles governing fine coal filtration has recently been recognised by the Australian coal industry as the most probable cause for the stagnation of dewatering technology and performance [1]. The current state of knowledge on vacuum filtration principles is not sufficient to assist industry in defining options for improving the performance of vacuum filters. Whether the performance currently achieved by vacuum filters is due to the inherent limitation of the filtration process remains to be answered. Hence, there is a growing urgency to understand the mechanisms that govern the rate of solids pick-up from fine coal slurries and those underlying cake moisture removal.

Fine coal dewatering, contrary to fine coal flotation, has not experienced any significant technical breakthroughs since the introduction of flocculant in fine coal washeries in the early 1970's. The higher recovery of fine and ultra-fine particles from newer and more efficient flotation technology has in fact made the inefficiencies of current dewatering technologies more apparent, and increased the need to understand and remedy the problems encountered in dewatering practice. A number of significant studies were commissioned in Australia in the late 1980's to investigate the influence of various dewatering parameters on filtration performance. One such study was by Clarkson et al. [2], who reviewed and correlated the effect of a large number of operating parameters – e.g., solids concentration, feed size distribution, and vacuum – on filtration performance. Such work has not however translated into significant transformation of dewatering practice, although it has been of considerable help from

an operational viewpoint by quantifying the effect of a range of operating parameters on filtration rate and product moisture.

The main reason that such pragmatic programmes of equipment assessment and development have not led to noticeable reforms in plant dewatering practice is probably because the fundamental mechanisms governing formation rate of and moisture removal from filter cakes remain poorly understood. Clarkson and Proud [1] concluded that one of the major research priorities in fine coal beneficiation was to explore the fundamental principles underlying coal water interactions. At the same time, it became apparent that the role played by cake microstructure in plant filtration performance needed to be investigated, and research efforts started on quantifying this role [3].

The objective of the work presented in this paper was to analyse critically the effect of both coal properties and filter cake microstructure on the filtration performance of bituminous coal fines (nominally -0.5 mm particles). Such an evaluation would permit quantification and comparison of their respective impacts on filtration performance, and ultimately identification of potential avenues for improving filtration performance of fine coal slurries. For the sake of clarity, the paper is divided into two sections that correspond to the two distinct areas of investigation, namely cake microstructure and coal properties.

THE ROLE OF CAKE MICROSTRUCTURE IN FILTRATION

Experimental Approach

The characterisation of cake microstructure relies on two principal investigate tools: a reliable filtration leaf test and an accurate technique for quantifying the three-dimensional microstructure of filter cakes.

The leaf test used in this study, which is referred to as the Single Leaf Filter Test of SLFT [4], enables the conduct of filtration tests under controlled and reproducible conditions as well as quantification of the macroscopic filtration properties of filter cakes. For instance, filter cake permeability can be routinely measured with a precision of $\pm 10^{-14}$ m², which is well suited for characterising typical fine coal filter cakes. Throughout this study, the SLFT was used to produce the filter cakes necessary for microstructure investigation. It is noted that the SLFT was developed to remedy the current absence of an Australian standard for fine coal filtration testing, which is a major handicap for dewatering research and plant design or upgrades. The filter cakes used in this work were produced using the SLFT in bottom-loading mode. In such a configuration, filter cakes that are produced resemble those of drum filters. The bottom-loading mechanism was perferred to the top-loading one because the latter induces a strong anisotropy in the filter cakes, as described by Binkley et al. [5]. Moreover, by combining such a cake formation mechanism with slurry flocculation, which narrows the apparent particle size distribution of the filtration feed, the filter cake microstructures exhibit little anisotropy in the direction of growth [3]. Once the cakes are formed, they are air-dried for approximately 24 hours and impregnated with a low-viscosity epoxy resin. Such a method permits consolidation of the filter cakes so that they can be subsequently sliced and ground to produce polished sections. The pore space is then imaged under ultra-violet illumination using a Quantimet microscope at a resolution of 1 µm per pixel. The binary structure of the filter cake cross-section images is quantified using a straightforward procedure that relies on well-documented mathematical theory [6]. The method [7] involves measuring the covariance function of the binary images. which yields a quantitative measure of the spatial correlation between the pore and solid phases of the filter cake microstructure. The covariance function is then described in terms of two morphological parameters that quantify precisely the three-dimensional microstructure of filter cakes.

Microstructure and Cake Formation Rate

Figure 1 shows the general correlation between cake permeability and filtration rate obtained for dewatering tests conducted with the SLFT unit on fresh filtration feeds of bituminous coals from Central Queensland washeries, Australia. It is noted that the general relationship between permeability and filtration rate holds over a wide range of operating conditions, as the data in Figure 1 were collected from a

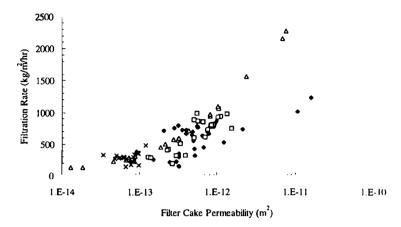


FIGURE 1 General relationship between filtration rate and cake permeability for a range of fine bituminous coal slurries. The symbols refer to different coal washeries where the data were collected.

large number of fine coal slurries under a wide range of conditions. This confirms that increasing cake permeability is the key to controlling and improving cake throughput.

The origins of the link between the permeability of the filter cake and the overall cake throughput of a plant are worth investigating. It has long been recognised [8] that the permeability of porous media such as filter cakes is controlled by the morphology of their pores. By means of image analysis of filter cake cross-sections, the microstructural properties of filter cakes can be revealed. The two cross-section images shown in Figure 2, in which the coal particles appear black and the pores white, are characteristic of filter cakes with low and high permeabilities. Such a microstructure can be accurately quantified with the Boolean model [7]. The Boolean process consists of implanting a given density of three-dimensional objects, or grains, with well-defined geometrical properties into space and produces a binary structure that is ideally suited for describing porous media. Bourgeois and Lyman [7] have shown that the three-dimensional microstructure of fine coal filter cakes can be accurately quantified by the Boolean process with Poisson polyhedra as primary grains. Both spatial density and geometrical properties of the grains in three-dimensional space can be measured from two-dimensional random cross-sections through a

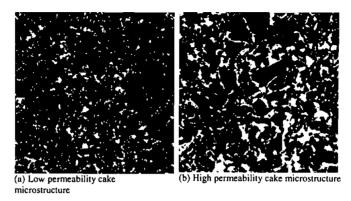


FIGURE 2 Cross-sections of filter cakes with low $(6.8 \times 10^{-13} \,\text{m}^2)$ and high $(70.4 \times 10^{-13} \,\text{m}^2)$ permeabilities (cross-section dimensions: 2.33 mm × 2.33 mm).

three-dimensional realisation of the Boolean process. It is important to note that the geometrical properties of the Poisson polyhedra are completely defined by a single parameter that is uniquely related to the mean volume of the Poisson polyhedra. Consequently, the complete three-dimensional characterisation of filter cake microstructures relies on two parameters only, the second parameter being the spatial density of the Poisson polyhedra. The variations of these parameters with filter cake permeability are plotted in Figure 3 for five distinct filter cakes. Although the number of data points is insufficient to describe with confidence the relation of three-dimensional microstructure with permeability, Figure 3 shows both a decrease in density of Poisson polyhedra and an increase in mean Poisson polyhedra volume with increasing filter cake permeability. This confirms the correlation between the three-dimensional properties of filter cake microstructure and filter cake permeability, and hence filtration rate.

Moreover, it is possible from two-dimensional considerations to relate the pore size with the flow that passes through filter cakes. If one assumes that microstructures such as those presented in Figure 2 extend in the direction perpendicular to the cross-section image, it is possible to calculate the flow in each individual capillary using a simple two-dimensional approach. Laminar flow in such capillaries is governed by Eq. (1)

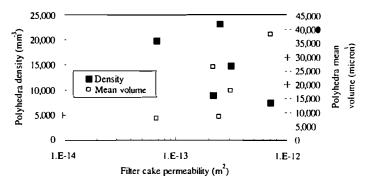


FIGURE 3 Variation of three-dimensional Boolean properties of fine coal filter cakes with permeability.

$$\nabla^2 w = \frac{1}{\mu} \frac{\partial P}{\partial z} \tag{1}$$

where w is the filtrate velocity in the z-direction, that is perpendicular to the filter cake cross section, $\partial P/\partial z$ is the applied pressure drop, and μ is the filtrate viscosity. The symbol ∇^2 is the Laplacian operator. Eq. (1) can be solved numerically using a finite difference method [9]. With the no slip assumption at the pore-particle boundary, the flow velocity field can be calculated directly from two-dimensional images of the filter cake microstructure. Figure 4 shows the outcome of such a calculation for the microstructures shown in Figure 2.

Conveniently, a different shade of grey is allocated for a given range of filtrate velocity w, allowing areas of fast flow to be easily identified. Figure 5 quantifies the fraction of the total flow rate that passes through the porous medium versus the pore cross-sectional area for the microstructures of Figure 2. For example, in the case of the microstructure shown in Figure 2b, this analysis (cf. Fig. 5b) reveals that the pores with cross-section larger than $10,000 \,\mu\text{m}^2$, which account for only 10% of the total pore cross-sectional area, carry over 90% of the flow. Figure 5a shows that for the fine microstructure of Figure 2a, pores larger than $1,000 \,\mu\text{m}^2$, which account for only 10% of the total cross-sectional porosity, carry over 60% of the total flow. Although present, this channelling effect is less important with the microstructure of Figure 2a, which is one order of magnitude less

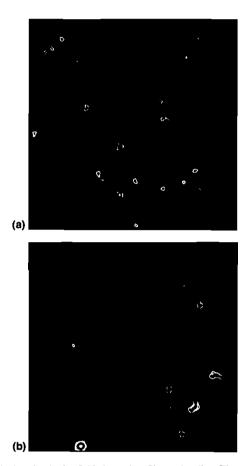
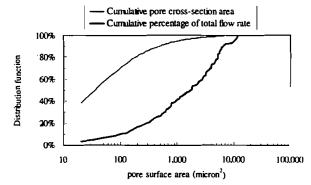
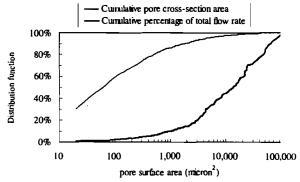


FIGURE 4 Calculated velocity field through a filter cake slice. The particles are black, and the brightness of the shade of grey within the pores is proportional to the filtrate velocity. a) Calculated flow in microstructure from Figure 2a; b) Calculated flow in microstructure from Figure 2b.

permeable than that of Figure 2b. Hence, filter cakes with high permeabilities are characterised by large conductive channels which control the rate at which filtrate can be drawn through the forming cake. It is noted that such large channels account for a small proportion of the total filter cake porosity. Such a result is consistent with Poiseuille's equation which states that flow rate through a duct varies with the fourth power of its radius. For practical vacuum filtration, maximising the channelling effect in filter cakes is clearly a



(a) Analysis of flow in microstructure of Figure 2a



(b) Analysis of flow in microstructure of Figure 2b

FIGURE 5 Quantification of the role of large channels on filter cake permeability.

means of improving the cake formation rate. It is interesting to note that proper flocculation of the filtration feed can produce such channelled and hence permeable microstructures [7].

Microstructure and Desaturation

Cake permeability not only dictates the rate of solids pick-up from a fine coal slurry, but also controls the kinetics of cake drainage to a large extent. Figure 6, obtained from the analysis of SLFT data, confirms that cakes with different permeabilities desaturate at different rates.

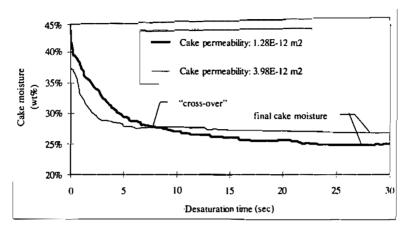


FIGURE 6 Experimental evidence of the effect of cake microstructure on desaturation kinetics and final cake moisture.

It is important to recognise that a high rate of desaturation does not necessarily lead to a low final cake moisture. Figure 6 also provides substantiating evidence that a cross-over can occur between desaturation curves, indicating that the cake with lower permeability in fact appears to dewater more thoroughly than the cake with the higher permeability. Note that it was ensured that the cakes, which were obtained under identical conditions using the SLFT apparatus, had identical heights and dry solids weights, confirming that the cross-over was really caused by differences in filter cake microstructure. This microstructural difference is supported by the variation in cake permeability. Figure 6 shows that cake microstructure also affects the equilibrium saturation [10], which is the lowest cake moisture that can be achieved for a given set of dewatering conditions. The physical reasons behind the effect of microstructure on equilibrium saturation are not yet clear. It is believed that cakes with high permeabilities experience very early air breakthrough across their large channels, which then short-circuits any further moisture removal. As discussed earlier, cakes with high permeabilities have large channels that account for only a small proportion of the total cake porosity. Hence, although such channels can desaturate rapidly and fully, the resulting cake moisture will be high due to the large amounts of water left behind in the filter cake pores. Such a conclusion is partly substantiated by

fundamental measurements of the properties of residual moisture in desaturated filter cakes (see the section on coal properties). Figure 6 also indicates that a relatively small change in microstructure, as indicated by the small variation in permeability, can have a substantial effect on filter cake desaturation behaviour.

Hence, filter cake microstructures that give high filtration rates and those that give low residual moistures are characterized by inherent morphological differences. This result explains at a fundamental level why current filtration technology can only attempt to achieve the best compromise between throughput and extent of dewatering. Since production is a priority for coal preparation plants, throughput is normally optimised at the expense of final cake moisture. The fact that current filtration technology does not permit dissociation of cake formation from cake drying cycles is therefore an inherent limitation of this technology, which could possibly be alleviated by decoupling the formation and drying phases of the fine coal filtration process.

THE ROLE OF COAL PROPERTIES IN FILTRATION

Experimental Procedures

Coal Samples

Samples of 12 Australian bituminous coals, mostly from the Bowen Basin (Queensland) but also from the Hunter Valley and Western Coalfield (New South Wales), were used in this study. The samples included both unwashed coals collected from the mine and washed products such as unflocculated filtration feed. Size and/or density fractions were separated from selected coals. Values of mean maximum vitrinite reflectance (R_v max) for the coals ranged from 0.65 to 1.65%. Ash yields did not exceed 20% (dry basis) and vitrinite contents varied between 18 and 94 vol% (mmf basis).

Nuclear Magnetic Resonance (NMR)

Two broadline proton NMR techniques, based on the measurement of time-domain transverse magnetisation signals, were used to investigate the properties of water associated with the coals. One of these techniques, initially reported by Lynch and Webster [11], quantifies the water whose thermodynamic properties are modified with respect to those of bulk water (due to interactions between the water and the coal) such that it does not freeze and melt at the temperatures of these phase transitions for bulk water. This form of water is hereafter referred to as non-freezing water. The second technique characterises water according to its proton spin-spin relaxation time which, for water confined within the voids of a porous solid, usually is found to decrease as the pore surface-to-volume ratio increases and as the interaction of water molecules with the solid surface becomes stronger [12]. All NMR measurements were conducted at a proton resonance frequency of 60 MHz.

Quantification of non-freezing water involved an NMR experiment in which the coal-water specimen was cooled to a temperature of -10° C or lower and then heated in steps to ambient temperature. NMR transverse magnetisation signals, in which the contribution from solid structures (e.g., coal and frozen water) is distinct from the contribution from liquid phases (e.g., water), were recorded during the heating regime and after allowing the specimen to reach thermal equilibrium at each temperature. In practice, non-freezing water was determined as the maximum water content of a coal for which there is no fusion transition in the vicinity of 0°C [13].

The intrinsic proton spin-spin relaxation behaviour for water associated with coal was characterized at room temperature by NMR spin echo techniques [14]. From the signals produced by all coal samples investigated, it was possible to distinguish two populations of water molecules with quite different relaxation behaviour [15]. These populations are hereafter referred to as rapidly-relaxing and slowly-relaxing water.

Most of the specimens used in the NMR experiments were prepared from air-dried coal with a nominal topsize no greater than 0.5 mm by adding the required amount of water to $\sim 200 \, \text{mg}$ of the coal in glass tube. The air-dried moisture contents were determined by drying separate subsamples at 105°C under nitrogen for $\sim 3 \, \text{hr}$. Immediately after preparation of the NMR specimens, the tubes were sealed with a flame.

There is evidence [16] that the interaction of water with coarse coal is reduced significantly if the coal has been partially dried and is then

rewetted. Comparison of fine coal specimens prepared by adding water to air-dried coal and by slowly reducing the moisture content of coal kept wet since collection to the desired value showed that prior air-drying reduces the level of non-freezing water by $< \sim 10\%$ and increases the spin-spin relaxation time only for slowly relaxing water.

Filter cake specimens were prepared by inserting cylindrical cores, taken from desaturated cakes, into glass tubes. The moisture contents of these NMR specimens, determined by drying the specimens after use, were very similar to the cake moisture values. Cores from desaturated filter cakes were resaturated by adding sufficient water to the NMR tubes to completely fill the interparticle voids within the specimens. Significant compaction of the cores obtained from flocculated filter cakes occurred during their insertion into the NMR tubes. Although this compaction had little effect on the NMR measurements on desaturated cake specimens (presumably because the voids that are easier to compress are the larger ones and thus are not filled with water), the water contents of the resaturated specimens would have been lower than those of the saturated filter cakes from which they were derived.

Gravimetric Sorption

The gravimetric sorption techniques involved the use of a state-of-the art Hiden Intelligent Gravimetric Analyser (IGA). This automated facility enables water adsorption/desorption isotherms to be recorded accurately for relative pressures of up to 0.9 and for temperatures between 5 and 40°C. Very good reproducibility is obtained for different subsamples of a given coal. These isotherms allow comparison of water uptake by different coals and by their constituent materials.

The classical Brunauer, Emmett and Teller (BET) sorption model [17] was applied to determine the number of water molecules required to produce statistical monolayer coverage of the coal surface. This quantity of water, derived from measurements at 26°C, is referred to hereafter as the monolayer water content. The isosteric net heat of adsorption was determined from the variation of relative pressure with temperature for a constant water uptake.

The coal specimens used for the gravimetric sorption experiments consisted of $\sim 200 \,\mathrm{mg}$ of material crushed to a topsize of 0.212 mm. Prior to exposure to water vapour, these specimens were thoroughly outgassed under a vacuum of 10^{-6} torr at $70^{\circ}\mathrm{C}$ (in most cases).

X-ray Photoelectron Spectroscopy (XPS)

As part of an investigation of the effects of oxidation of fine coal on its filtration behaviour, XPS measurements were conducted on single particle specimens prepared to be as representative as possible of the fine coal used in the filtration experiments. These specimens were placed in an air-flow oven with the fine coal and oxidised at 70°C and ambient relative humidity of one week. C 1s spectra of sufficiently narrow linewidth to enable comparison of the concentrations of surface carbon-oxygen functional groups were recorded before and after this oxidative treatment.

The Extent of Coal-Water Interactions

The influence of the nature of the coal material on its associated water is expected to be greatest for water closest to the surface of the coal particles. For particles larger than $\sim 1 \, \mu m$, the external surface area is much less than the surface area of the internal pore structure. Therefore the water which interacts most strongly with the coal resides mostly within the particles. Because this water is not removed by mechanical dewatering processes, variations in the quantity of this water between different coals may be reflected in the steady-state residual moisture obtained for a given process. For example, SLFT experiments conducted under very similar feed and operating conditions on two bituminous coals of different rank (R_v max values of ~ 0.9 and $\sim 1.5\%$) produced residual cake moisture values which were consistently at least 5% higher for the lower-rank coal than for the higher-rank coal. Considerable differences between the two coals were also observed in cake formation rate as a function of flocculant conditioning time.

The nuclear magnetic resonance (NMR) and gravimetric sorption techniques described in the Experimental Procedures section provide the following measures of the extent of interaction of water with bituminous coals:

- a) non-freezing water, which is defined as water whose thermodynamic properties are modified with respect to those of bulk water such that it does not undergo a fusion transition on heating through 0°C.
- b) rapidly-relaxing water, which refers to a population of water molecules distinguished from other water associated with the coal by a much shorter proton NMR spin-spin relaxation time.
- c) monolayer water, defined as the quantity of water required to completely cover the coal surface with a single layer of molecules, as determined by BET analysis of water adsorption data.

It should be noted that monolayer water is a statistical quantity because the actual distribution of water molecules on the coal surface is not uniform due to the heterogeneous nature of the surface. These three water quantities occur mostly within the intraparticle pore structure and are related in that, for the coals studied, rapidly-relaxing water corresponds to approximately two statistical monolayers on the coal surface whereas non-freezing water is equivalent to about / 5 such monolayers. For a number of the coals, non-freezing corresponds closely to equilibrium water uptake at a relative r of ~ 0.9 . Becuase of these relationships, the following discurfocus mainly on the largest of the three water quantities, i.e. freezing water.

Values for non-freezing water in the set of bituminous coals studied range from 2.6 to $> \sim 8$ wt %. For coals with R_{ν} max > 1%, the values are in the vicinity of 3 wt %. Lower-rank coals have larger and more variable values. The difference in non-freezing water (~ 3 wt %) between the two coals used in the SLFT experiments referred to above can partly account for the difference in residual cake moisture values. Figure 7 shows that, for coals with oxygen contents $> \sim 4$ % (daf) (as determined by difference from ultimate analysis), non-freezing water correlates linearly with the oxygen content. Moreover, for a given water uptake per unit weight of coal, the net heat of water adsorption also increases with increasing oxygen content. These results indicate, in agreement with earlier reports in the literature (see, for example, [18, 19]), that the concentration of oxygen-containing functional groups on the coal surface is an important factor in determining the extent of interaction of water with bituminous coals.

Another possible explanation for the dependence of coal-water interactions on oxygen content is that the surface area of the internal

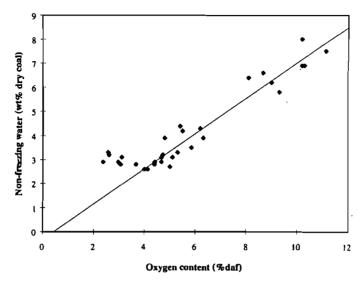


FIGURE 7 Variation of non-freezing water with oxygen content for the bituminous coals studied. The linear regression for coals with $> \sim 4$ wt. % oxygen (daf) is also shown.

pore structure of coals increases with decrease in rank and thus increase in oxygen content. However, the fact that non-freezing water correlates more strongly with oxygen content than with other rank parameters indicates that the composition, rather than the extent, of the coal surface is more important for its interaction with water.

A detailed investigation of two bituminous coals with $R_v \max \sim 1.1\%$ has shown that both water uptake at 26°C and non-freezing water are enhanced by the presence of clay minerals such as kaolinite and montmorillonite. This influence of mineral matter is expected to be less significant for lower-rank bituminous coals because the organic material in these coals has the capacity to interact with a greater quantity of water.

There is no indication from the data obtained in this study for higher-rank bituminous coals that the water quantities defined above are influenced significantly by maceral composition. However, in a lower-rank bituminous coal $(R_v \max = 0.65\%)$, vitrinite macerals appear to contain more non-freezing water than inertinite macerals.

There is evidence from previous work that the low-temperature oxidation of a coal has a deleterious effect on its dewatering response [20, 21]. A possible mechanism for this effect is a reduction in

hydrophobicity which occurs as a result of an increase in the surface concentration of carbon atoms that are bonded to oxygen atoms. In an effort to confirm the findings of previous work and to clarify the mechanism, oxidation experiments were conducted in which two higher-rank bituminous coals were exposed to ambient air at 70°C for one week. This resulted in a marked increase in the surface concentration of carbon-oxygen functional groups as determined by Xray photoelectron spectroscopy [22]. Evidence was found of a further enhancement in the concentration of these functional groups when the coal is brought into contact with liquid water after exposure to air. However, filtration tests conducted on unflocculated slurry using the SLFT unit in top-fed configuration were unable to detect any significant effect of oxidation on either filtration rate or residual cake moisture. Small effects observed, e.g., and increase of ~ 1.5 wt % in residual cake moisture after oxidation, were comparable to the repeatability of top-fed test results. It was also found that the oxidation treatment had little effect on the interaction of water with the coal as measured by water uptake or the quantity of non-freezing water. In view of the strong correlation between non-freezing water and coal oxygen content (Fig. 7), no satisfactory explanation can be offered for this insensitivity of water properties to coal surface composition modified by exposure to air at moderately elevated temperatures.

Variations in hydrophobicity also occur between coals because of differences in the concentration and nature of inherent oxygen-containing functional groups at the surface. However, from the foregoing discussion, the effect of these variations on residual moisture in fine coal filter cakes is expected to be small and thus difficult to detect. For coarse coal, hydrophobicity has been found to have a significant influence on the moisture content after centrifugation [23]; this may be due to the much lower dewatered moisture levels attained.

NMR Relaxation Behaviour

NMR measurements on fine coal specimens show that the average relaxation time for the interparticle water increases markedly as the content of this water increases but, at water contents typical of those in desaturated filter cakes (i.e., 20-25 wt %), is still much shorter than the relaxation time for bulk water. The relaxation process becomes faster with both decreasing particle size and increasing breadth of the

size distribution. These results are consistent with the expectation that, for a given coal, the water relaxation time increases with decreasing surface-to-volume ratio (and hence increasing size) of the interparticle voids that are filled with water. The observation that interparticle water usually has a distribution of relaxation times is a consequence of the existence of water-filled voids with a distribution of sizes. Because water relaxation and ease of dewatering are influenced in qualitatively similar ways by particle size and size distribution. NMR relaxation techniques have the potential to provide valuable insights into fine coal filtration.

This has been demonstrated by the use of this NMR approach to characterise residual water in filter cake specimens of a column cell concentrate from a high-rank bituminous coal (R_v max = 1.54%) after desaturation for a period of one minute. The filter cakes were prepared by the SLFT in bottom-fed configuration from slurries treated with different doses of anionic flocculant (up to 80 g/tonne) for conditioning times between 1 and 15 min. The average NMR relaxation time of the residual interparticle water in these specimens was found to correlate significantly with the permeability (and hence the microstructure) of the filter cakes as determined by filtration tests (Fig. 8). This novel

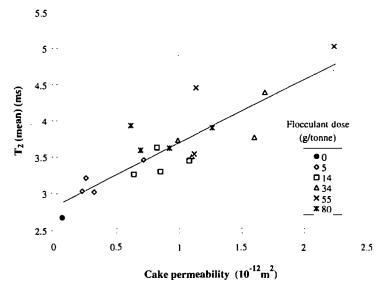


FIGURE 8 Correlation between average relaxation time T_2 (mean) for residual moisture in desaturated filter cake specimens and cake permeability for a high-rank bituminous coal. Specimens from cakes prepared with different flocculant doses are distinguished.

result indicates that water remains in larger interparticle voids, on average, after desaturation of the more permeable cakes and suggests that these cakes have greater potential for further moisture removal which may be limited, in practice, by earlier air breakthrough than for less permeable cakes.

A significant correlation between water relaxation time and cake permeability was also obtained for the filter cake specimens after resaturation. This relationship presumably arises from the fact that both parameters depend on the size of water-filled voids which in turn is influenced by the flocculation treatment. These results illustrate the potential of NMR relaxation techniques for providing a relative measure of the ease of cake desaturation.

Efforts have also been made to compare the relaxation of water in beds of fine particles of similar size from different coals and hence to assess the possible influence of coal properties on the behaviour of interparticle water. For water in beds of $-0.106+0.075\,\mathrm{mm}$ size fractions of three bituminous coals, the average relaxation time at a given level of interparticle water differs considerably and is longer for higher rank, and hence greater expected hydrophobicity, of the coal (Fig. 9). Although the NMR specimens were prepared by adding water to air-dried size fractions of the coals, the differences between the

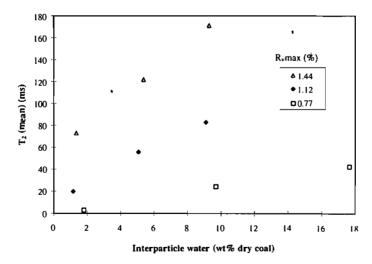


FIGURE 9 Comparison of the average relaxation time T_2 (mean) for interparticle water associated with three bituminous coals and plotted against the quantity of this water.

relaxation time values for the three coals are too large to be attributed to the effects of air-drying and then rewetting the specimens. However, measurements on samples of a larger set of bituminous coals (which should be kept wet between collection and testing) are required to confirm the rank dependence found here for the NMR relaxation behaviour of interparticle water.

CONCLUSIONS

This study has led to the conclusion that filter cake microstructure dominates the kinetics of both cake formation and cake desaturation. Coal surface and bulk properties probably have little effect on the kinetics of these processes. Figure 10 provides a conceptual tool to

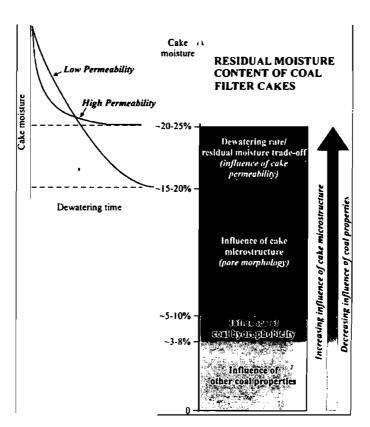


FIGURE 10 Conceptual model for residual moisture content in fine coal filter cakes.

help visualise the extent of influence of the various cake and coal properties on residual cake moisture. It is important to note that not only filter cake microstructure but also coal properties have a significant influence on the retention of moisture by filter cakes. In some bituminous coals, as much as 40% of the residual cake moisture cannot be removed by conventional mechanical means because it is trapped largely within the internal pore structure of the coal particles.

In light of these findings, understanding and controlling the microstructural properties of fine coal filter cakes appears to be a pre-requisite for improving filtration technology, so that it is better adapted to today's more efficient coal preparation plants. However, the results obtained in this study indicate that there does not exist a single microstructure capable of providing both a high filtration rate and a low product moisture.

Future research efforts need to be directed towards understanding the effect of particle flow on cake morphology, in order to enhance the channelling effect responsible for high filtration rates. Moreover, to satisfy the urgent need to reduce cake moisture, either a means of altering the morphology of the filter cake between the formation and the drying cycles or design of novel technology that allows the formation and drying phases to be decoupled, is required.

Acknowledgements

This work was largely conducted as part of the Coal Processing research programme of the Cooperative Research Centre for Mining Technology and Equipment (CMTE). The participants are the Australian Mineral Industries Research Association (AMIRA), CSIRO and the University of Queensland. The financial support of the Australian Coal Association Research Program (ACARP) is also acknowledged.

The authors also wish to acknowledge the valuable assistance and strong support of personnel based at plant sites. Invaluable contributions to this study were made by Dr Chris Clarkson, Dr Geoffrey Lyman, Dr John Davis and Ms Elaine Wightman at the University of Queensland, and by Dr Alan Buckley, Mr Alan McCutcheon, Mr Ralph Tyler, Ms Josephine Cheng and Mr Neil Thomas at CSIRO.

References

- [1] C. J. Clarkson and D. Proud, ACARP Sponsored Study into Established Priorities for Coal Dewatering Research and Development; Carbon Consulting International Pty Ltd. 1993.
- [2] C. Clarkson, V. Fiedler, T. Nicholson and D. Hornsby, Vacuum Filtration of Fine Coal by Disc Filter - A Pilot Study, in *Proceedings of the Fourth Australian Coal Preparation Conference*, 6A, pp. 261-286 (1988).
- [3] Rui Zhu, Dewatering of Fine Coal and Tailings, JKMRC/AMIRA Project P239A Progress Report, Chapter 4, pp. 180-195 (1993).
- [4] F. Bourgeois, E. Wightman, C. Clarkson, Zhu Rui, M. Hilden and J. Davis, A New Benchmark Single Leaf Filtration Test for Fine Coal Dewatering, in *Proceedings of the Seventh Australian Coal Preparation Conference* (J. Smitham, Ed.) Australian Coal Preparation Society, pp. 177-199 (1995).
- [5] T. O. Binkley, R. Venkatadri, G. E. Klinzing and S. H. Chiang, Effect of Surfactant Washing on Enhanced Dewatering of Fine Coal, in *Particulate and Multiphase Processes*, 3 (T. Ariman and T. N. Vezisoglu, Eds.), Hemisphere Publishing Co., New York, pp. 373-390 (1987).
- [6] J. Serra, Image Analysis and Mathematical Morphology, Academic Press, London (1982).
- [7] F. Bourgeois and G. Lyman, Morphological Analysis and Modelling of Fine Coal Filter Cake Microstructure, *Chemical Engineering Science*, **52**/7, 1151-1162 (1997).
- [8] F. A. L. Dullien, Porous Media: Fluid Transport and Pore Structure, 2nd edition, Academic Press Inc. 1992.
- [9] P. Roache, Computational Fluid Dynamics, Hermosa Publishers, 1992.
- [10] R. J. Wakeman, The Prediction and Calculation of Cake Dewatering Characteristics, Filtration and Separation, 16, 655-669 (1979).
- [11] L. J. Lynch and D. S. Webster, Effect of Thermal Treatment on the Interaction of Brown Coal and Water: A Nuclear Magnetic Resonance Study, Fuel, 61, 271 – 275 (1982).
- [12] W. P. Halperin, F. D. Orazio, S. Bhattacharja and J. C. Tarczon, Magnetic Resonance Relaxation Analysis of Porous Media, in *Molecular Dynamics in Restricted Geometries* (J. Klafter and J. M. Drake, Eds.) John Wiley, New York, pp. 311-350 (1989).
- [13] W. A. Barton and L. J. Lynch, Coal Inherent Moisture Its Definition and Measurement, in *Proc. 6th Australian Coal Science Conf.*, Australian Inst. of Energy, Newcastle, pp. 65-72 (1984).
- [14] C. P. Slichter, *Principles of Magnetic Resonance*, Second revised and expanded edition, Springer-Verlag, Berlin, 1980.
- [15] W. A. Barton and J. Y. Cheng, Characterisation of Water in Coal Particle Beds by Nuclear Magnetic Resonance Techniques, in *Proc. 7th Australian Coal Science Conf.*, Australian Inst. of Energy, Gippsland, pp. 521-528 (1996).
- [16] E. T. White, L. K. Kaiser, Y. He, B. Jensen, B. R. Stanmore and B. A. Firth, An Approach for the Laboratory Investigation of Coarse Coal Dewatering by Centrifugation, Coal Preparation, 17, 47-59 (1996).
- [17] S. J. Gregg and K. S. W. Sing, Adsorption, Surface Area and Porosity, 2nd edition, Academic Press, London, 1982.
- [18] J. S. Laskowski, Coal Surface Chemistry and its Role in Fine Coal Beneficiation and Utilization, Coal Preparation, 14, 115-131 (1994).
- [19] T. P. Maher and W. A. Barton, A Review of Literature on Water in Coal, Investigation Report CET/IR456, CSIRO Division of Coal and Energy Technology, North Rvde. 1996.
- [20] L. F. Dolina, Influence of Rank and Degree of Oxidation of Coal on Dewatering, Coke Chem. USSR, 7, 8-10 (1973).

- [21] D. W. Fuerstenau and J. Diao, Characterization of Coal Oxidation and Coal Wetting Behavior by Film Flotation, Coal Preparation, 10, 1-17 (1992).
- [22] A. N. Buckley and R. N. Lamb, Surface Chemical Analysis in Coal Preparation Research: Complementary Information from XPS and ToF-SIMS, *Inter. J. Coal. Geology*, 32, 87-106 (1996).
 [23] B. A. Firth, E. T. White, B. Jensen, B. R. Stanmore, Y. He and M. O'Brien,
- [23] B. A. Firth, E. T. White, B. Jensen, B. R. Stanmore, Y. He and M. O'Brien, Factors Influencing the Moisture Content of Coarse Coal after Centrifugation, Coal Preparation, 17, 117-136 (1996).