Washing of the Liquid Retained by Granular Solids

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A mathematical model termed the *blind side channel* model is developed to describe the washing performance of liquid retained in a bed of granular solids. The effects of operating variables and system's parameters, such as the flow rate of wash liquor, the diffusivity of the liquid system, and the thickness of the bed, are discussed. The experimental washing study was carried out with granular solids such as glass beads, sand, and crystalline solids, and application of wash liquors miscible in all cases with the residual liquid in the bed, drained by centrifuging. Results from the developed model showed very good agreement with the experimental results. The developed model would be valuable in analyzing the washing performance for process improvement and in designing washing systems.

The removal of the residual liquid from the filter cakes, called washing, is one of the common unit operations in the chemical industry. The liquid is held in drained or centrifuged filter cakes mainly by surface tension forces.

Mathematical analysis of mass transfer between the filtrate and wash has been tried by several authors. Rhodes (*1*) presented a performance equation of this general type and correlated it with certain data for sodium chloride washing, assuming that the wash liquor was perfectly mixed with the filtrate so that the mass transfer coefficients did not appear explicitly. His performance equation was accordingly a simple exponential decay in solute concentration with time. It was developed for application to the washing of a saturated bed having voids full of filtrate. His equation fits the experimental data well when the washing operation is under way, but it fails to describe the initial piston-like displacement of filtrate at the beginning of the wash. Kuo (*2*) assumed that before the start of a wash cycle most of the filtrate has been forced out of the filter cake pore spaces by the pressure difference across the filter cloth and that a channel for the flow of wash liquor is formed, with a stagnant film of filtrate remaining on its surface. The washing serves to extract the remaining solute from this film. He presented transport equations that were derived by assuming that plug flow occurs in the pores of a filtered bed, with continuous mass transfer from a film of filtrate to the wash liquor. The differential equations and their solutions represent a more elegant treatment of the washing operation than those previously available. Dobie (*3*) set up a system equation for the diffusion operation and got a washing efficiency chart, by assuming that the cake forms a bundle of capillaries, that all the pores of the cake are accessible to the wash liquor, and that no viscous fingering occurs between the wash liquor and filtrate. These earlier analyses appear to be too simplified, because the flow channel in the packed bed does not consist of a simple bundle of capillaries, even in the simple case of a bed of spheres of uniform size. Most of the filtrate is retained in the interstices of the particles, in what may be represented by blind side channels, and not in the straight channels along whose walls there are many pores. Brenner (*4*) presented the solution of the diffusion model of miscible fluid displacement in beds of finite length. But the applicability of his solution to the washing of filter cakes appears to be doubtful because his model did not describe the mechanism of solute displacement by wash liquor. Turner (*5*) presented an analysis of flow structure of a system and showed how the frequency response technique might be used to analyze the flow structure in a packed bed in terms of simplified models. His model 1 assumes that each flow channel is connected with pockets of given length in which molecular diffusion but no flow takes place, and his model 2 assumes that there is a distribution of side channels of different radii and length in which axial dispersion and flow take place. Turner's model assumes a uniform cross-sectional shape and area of side pockets. Aris (*6*) extended Turner's analysis to a more generalized model. He presented a solution of the integral equation in the form of a definite integral. Gottschlich (*7*) reported an analysis similar to Turner's, investigating the axial dispersion in a packed bed. Recently Ananthakrishnan et al. (*8*) presented exact numerical solutions to the extended Taylor-Aris theory with both axial and radial molecular diffusion accounted for. Sherman (*9*) analyzed the washing of saturated bed of beads and fibers with a longitudinal dispersion model. However he, as the other authors (*1, 3, 4*), did not consider the mechanism of liquid displacement between the wash liquor and filtrate in the interstices of the particles in a bed of granular beads. He also considered a bed of porous particles (in his case of fibrous media) with the assumption that the quantity of solute sorbed by the solid per volume of solid is proportional to the concentration of solute in the flowing liquid through the bed. This assumption is, however, subjected to a serious consideration. A theory of such a bed of porous structure of materials is developed by Han (*10*) with an extension of the same idea presented in this paper.

In the work presented here we considered the case that the bed of granular solids reached residual equilibrium and a mathematical model, termed the *blind side channel* model, has been described and developed. Two types of the blind side channel model have been considered on

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the basis of the cross-sectional area across which diffusion might occur: model 1, uniform cross-sectional area of the blind side channel; and Model 2, varying cross-sectional area which is a function of channel distance. An experimental washing study was carried out using glass beads, sand, and crystals as granular solids and applying wash liquors miscible in all cases with the residual liquid in the bed, drained by centrifuging.

DEVELOPMENT OF THE MATHEMATICAL MODEL BLIND SIDE CHANNEL MODEL

In the following derivation the volume of the interstices of the particles is defined by a system of blind side channels which retain residual liquid that is not drained by mechanical means, and the volume of the void channels through which wash liquor flows is defined by a system of straight channels. For laminar flow the wash is assumed to follow the straight channel without axial mixing but not to enter the side channels where residual liquid is retained, because the liquid retained in the side channels is assumed to exist in the dead space.

In order to set up a material balance for the residual liquid after wash is applied to the system, we may have two equations: one for the side channel and the other for the straight channel. The solutions are obtained for different cases by the Laplace transform technique and the desired final equation, which represents the fraction of the residual liquid washed during a certain washing period, is obtained by the use of our definition of the relationship between the geometry of the bed and the residual equilibrium saturation.

Derivation of System Differential Equations

Consider that the bed is drained by either gravitational or centrifugal forces before washing starts. Filtrate may be retained either in both the straight and blind side channels when gravity is applied to the bed of small granular particles or only in the blind side channels when centrifugal force is applied to the system. This also depends upon the particle sizes and the properties of the filtrate. Centrifuges are commonly employed in industry for draining the bed of crystals. Therefore let us focus our attention on centrifugal drainage in deriving the differential equations. The following assumptions are made in the derivation:

1. Solute exists only in all blind side channels before washing starts.
2. Solute in the blind side channels is displaced by molecular diffusion into the wash stream in the straight channels after washing starts.
3. Once solute in the blind side channels diffuses out of the pores, it is carried down the bed by the wash liquor flowing down the straight channels with plug-flow velocity profile.

With these assumptions, let us define the system and set up the system's equations. Referring to Figure 1, we have vertical straight channels along whose walls there are many side channels. At time $t = 0$, the side channels are either totally or partially full of residual liquid, depending on the system used and conditions of draining. These two cases give us different initial conditions which will be considered separately in solving the differential equations.

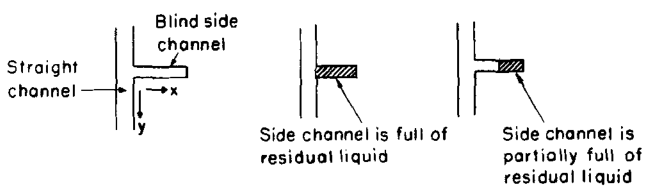

Fig. 1. Geometry of the blind side channel.

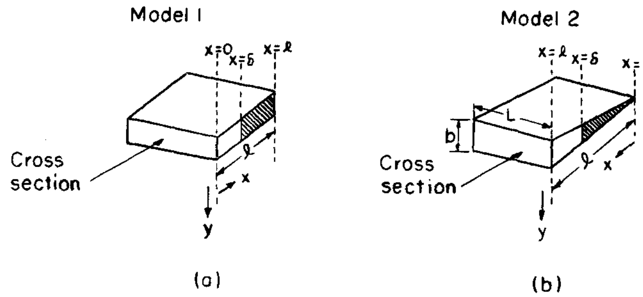

Fig. 2. Two different models of the blind side channels.

Writing the material balance for residual liquid in the straight channel in $(y, y + \Delta y)$ during $(t, t + \Delta t)$ for $0 < y < vt$, we get

$$\frac{\partial \mu}{\partial t} + V\frac{\partial \mu}{\partial y} = aN \tag{1}$$

The boundary conditions for Equation (1) are

$$\mu(t, y) = 0 \qquad \text{for } t > y/v \text{ and } y = 0 \tag{2}$$

$$\mu(t, y) = 0 \qquad \text{for } y > 0 \text{ and } 0 \leq t \leq y/v \tag{3}$$

In solving Equation (1), N must be obtained from another relationship which describes the concentration profile in the blind side channels as a function of time and axis x, whose direction is perpendicular to the axis y of the straight channel. This relationship comes from assumption 2, that molecular diffusion governs the concentration profile in the blind side channels.

Model 1. Uniform Cross-Sectional Area of the Blind Side Channels. The material balance for solute in the blind side channel (see Figure 2*a*) yields

$$\frac{\partial C(\theta, x)}{\partial \theta} = D\frac{\partial^2 C(\theta, x)}{\partial x^2} \tag{4}$$

The boundary conditions for Equation (4) are:

$$C(\theta, x) = C_o, \quad \text{at } \theta = 0, \text{ and } \delta \leq x \leq l \tag{5}$$

$$C(\theta, x) = 0 \quad \text{at } \theta = 0, \text{ and } 0 \leq x < \delta \tag{6}$$

$$\frac{\partial C(\theta, x)}{\partial x} = C \quad \text{at } x = l, \ \theta > 0$$

$$\text{for finite length of side channel} \tag{6}$$

$$C(\theta, x) = \rho(\theta, y) \quad \text{at } x = 0 \tag{7}$$

The time θ in Equation (4) is different from time t in Equation (2), because filtrate in the blind side channel starts to diffuse after the slug of wash reaches the height of each blind side channel. Therefore θ has a time delay y/v relative to t, actual time of washing, for any value of y, that is

$$\theta = t - y/v \tag{8}$$

Model 2: Varying Cross-Sectional Area of the Blind Side Channels. The material balance for solute in the blind side channel (see Figure 2*b*) yields

$$B(x)\frac{\partial C(\theta, x)}{\partial \theta} = D\frac{\partial}{\partial x}\left\{B(x)\frac{\partial C(\theta, x)}{\partial x}\right\} \tag{9}$$

where the cross-sectional area is given by

$$B(x) = bLx/l \tag{10}$$

As shown in Figure 2b, the direction of the x axis in model 2 is chosen opposite to that in model 1, solely for convenience in mathematical manipulation.
The boundary conditions for Equation (9) are

$$\begin{aligned} C(\theta, x) &= C_o \quad \text{at } \theta = 0, \text{ and for } 0 \leq x < \delta \\ C(\theta, x) &= 0 \quad \text{for } \delta \leq x \leq l \end{aligned} \tag{11}$$

$$\frac{\partial C(\theta, x)}{\partial x} = 0 \quad \text{at } x = 0 \text{ and } \theta > 0 \tag{12}$$

$$C(\theta, x) = \rho(\theta, y) \quad \text{at } x = l \tag{13}$$

Solution of System Differential Equations

Changing the variables with

$$\begin{cases} \theta = t - y/v \\ \rho(\theta, y) = \mu(t, y) \\ M(\theta, y) = N(t, y) \end{cases} \tag{14}$$

and substituting from Equation (14) into Equation (1), we get

$$\frac{\partial \rho(\theta, y)}{\partial y} = \frac{a}{v} M(\theta, y) \tag{15}$$

Model 1: Uniform Cross-Sectional Area of the Blind Side Channels. The flux of solute from the blind side channels into wash liquor, M in Equation (15), is related to Equation (4) by

$$M(\theta, y) = D \left. \frac{\partial C(\theta, x)}{\partial x} \right|_{x=0} \tag{16}$$

The system of Equations (4) and (15) with the relation (16) is solved by use of the Laplace transform yielding

$$\bar{\rho}(p, y) = \frac{C_o \sinh\{\alpha(l - \delta)\}}{p \sinh(\alpha l)} \{1 - \exp[-Y\beta(p)]\} \tag{17}$$

where

$$\alpha = \sqrt{p/D}$$

$$\beta(p) = \sqrt{\frac{p}{D}} \tanh\left(\sqrt{\frac{p}{D}}\, l\right)$$

$$Y = aDy/v$$

The bar in Equation (17) indicates a Laplace transformed variable. When the side channels are full of solute before washing starts, that is, at $\delta = 0$, we obtain

$$\bar{\rho}(p, y) = \frac{C_o}{p} \{1 - \exp[-Y\beta(p)]\} \tag{18}$$

Model 2: Varying Cross-Sectional Area of the Blind Side Channels. The system of Equations (9) and (15) with the relation

$$M(\theta, y) = D \left. \frac{\partial C(\theta, x)}{\partial x} \right|_{x=l} \tag{19}$$

is solved by use of the Laplace transform, yielding

$$\bar{\rho}(p, y) = \frac{C_o I_1(\alpha\delta)}{p\, I_1(\alpha l)} \{1 - \exp[-y\gamma(p)]\} \tag{20}$$

where

$$\alpha = \sqrt{p/D}$$

$$\gamma(p) = \sqrt{p/D}\, I_1(\sqrt{p/D}\, l)/I_o(\sqrt{p/D}\, l)$$

$$y = aDy/v$$

When the side channels are full of filtrate before washing starts, letting $\delta = l$ (see Figure 2b) yields

$$\bar{\rho}(p, y) = \frac{C_o}{p} \{1 - \exp[-y\gamma(p)]\} \tag{21}$$

It can be seen that both Equations (18) and (21) have an infinite number of first-order poles along the negative real axis. Except for these poles, $\beta(p)$ in Equation (18), for instance, is analytic throughout the p plane. In particular, $\beta(p)$ is analytic in the half plane. In view of these properties the function $e^{-Y\beta(p)}/p$ has an essential singularity at each pole of $\beta(p)$ and is analytic everywhere else and $\gamma(p)$ of Equation (21) is similar to $\beta(p)$ of Equation (18). Because an infinite number of essential singularities exist, the usual method of the inverse Laplace transform by residues is not practical for Equations (18) and (21). Since the Padé approximation, defined by

$$e^{-Y\beta(p)} = \left(1 - \frac{Y\beta(p)}{2}\right) \Big/ \left(1 + \frac{Y\beta(p)}{2}\right) \tag{22}$$

did not appear to offer any advantages due to the functional form of $\beta(p)$, the first-order approximation by Taylor's series expansion was adopted to Equations (18) and (21) to yield

$$\bar{\rho}(p, y) = \frac{C_o a\sqrt{D}y}{v\sqrt{p}} \tanh\left(\sqrt{\frac{p}{D}}\, l\right) \tag{23}$$

from Equation (18) for model 1, and

$$\bar{\rho}(p, y) = \frac{C_o a\sqrt{D}y}{v\sqrt{p}} \frac{I_1(\sqrt{p/D}\, l)}{I_o(\sqrt{P/D}\, l)} \tag{24}$$

from Equation (21) for model 2.

The inverse Laplace transform of Equations (23) and (24) results in

$$\mu(t, y) = \begin{cases} \dfrac{2C_oADy}{Ql} \displaystyle\sum_{n=1}^{\infty} \exp\left\{-\dfrac{D\left[\left(n - \frac{1}{2}\right)\pi\right]^2 (t - y/v)}{l^2}\right\}; & \text{for } t > y/v \\ 0 & \text{for } 0 \leq t \leq y/v \end{cases} \tag{25}$$

in which n is an integer, and

$$\mu(t, y) = \begin{cases} \dfrac{2C_oADy}{Ql} \displaystyle\sum_{n=1}^{\infty} \exp\left\{-\dfrac{D\beta_n^2(t - y/v)}{l^2}\right\}; & \text{for } t > y/v \\ 0, & \text{for } 0 \leq t \leq y/v \end{cases} \tag{26}$$

in which β_n are the roots of the first kind of zero-order Bessel function, J_o, respectively.

The concentration, as obtained in Equations (25) and (26), may not be a convenient way of comparing the computed with the experimental results. Therefore the expression which gives the fraction of the residual liquid removed from the side channel for a certain period of washing or for a certain volume of wash liquor used can be obtained by

$$F = \int_{y/v}^{t} (\mu(s, y)/C_o)\, Q\, ds/\epsilon VR \qquad (27)$$

where s is a dummy variable. Integration of Equation (27) after the substitution of Equation (25) into Equation (27) yields

$$F_1 = \frac{2Ayl}{\epsilon V\pi^2 R}\sum_{n=1}^{\infty} \frac{1}{\left(n-\frac{1}{2}\right)^2}\left\{1 - \exp\left[-\frac{\left(n-\frac{1}{2}\right)^2 D\pi^2(t-y/v)}{l^2}\right]\right\} \qquad (28)$$

and substitution of Equation (26) into Equation (27) yields

$$F_2 = \frac{2Ayl}{\epsilon VR}\sum_{n=1}^{\infty}\frac{1}{\beta_n^2}\left\{1 - \exp\left[\frac{D\beta_n^2(t-y/v)}{l^2}\right]\right\} \qquad (29)$$

Scheme of Computation and Variables

Numerical computation was carried out for Equations (25), (26), (28), and (29) with the following variables: height of packing, flow rate of wash liquor, washing period, diffusivity of the residual liquid and wash liquor, porosity of the bed, length of blind side channel, and fraction of the blind side channel initially filled with the residual liquid. In order to carry out the numerical computation with the derived equations, we have to define and determine a few system's parameters, based on the physical situations and experimental results, if necessary.

It is a difficult problem to define the length of the blind side channel and the pore area at the entrance of the blind side channel. It may be expected that there are some relationships between the residual equilibrium saturation and the geometry of the side channel (length and pore area). From the definition of residual saturation R, we have a relation:

$$\frac{R}{1-R} = \frac{\text{residual volume/void volume}}{1 - \dfrac{\text{residual volume}}{\text{void volume}}} = \frac{\text{volume of residual liquid}}{(\text{void volume} - \text{residual volume})}$$

$$= \frac{\text{volume of residual liquid}}{(\text{volume of straight channel} + \text{volume of side channel unfilled})}$$

Model 1: Constant Cross Section of the Blind Side Channel. The following relationship is found by referring to Figure 2*a*:

$$\frac{(l-\delta)a}{1+\delta a} = \frac{\text{residual volume/volume of straight channel}}{\left(1 + \dfrac{\text{volume of unfilled side channel}}{\text{volume of straight channel}}\right)}$$

$$= \frac{\text{residual volume}}{(\text{volume of straight channel} + \text{volume of side channel unfilled})}$$

where

$$a = \frac{Av}{Q} = \frac{\text{sq.ft. of pore area}}{\text{cu.ft. of straight channel}}$$

From the above relation one obtains

$$\frac{R}{1-R} = \frac{(l-\delta)a}{1+\delta a} \qquad (30)$$

For a given value of R (from experiment) two of the three variables (l, δ and a) can be chosen arbitrarily. When all side channels are filled with the residual liquid before washing starts ($\delta = 0$), the length of the side channel l can be determined since the ratio of the area of pore to the volume of straight channel a is related to l by

$$\frac{R}{l(1-R_o)} = \frac{\text{pore area of side channel}}{\text{volume of straight channel}} = a = \frac{Av}{Q} \qquad (31)$$

where R_o is the residual saturation at $\delta = 0$ and v is the average velocity of wash liquor based on the void cross-sectional area given by

$$v = \frac{Q}{A_c\epsilon(1-R_o)} \qquad (32)$$

Thus one obtains

$$A = R_o\epsilon A_c/l \qquad (33)$$

From Equation (33) A could be determined by knowing l or vice versa, provided R_o is measured by experiment. As a practical procedure of determining the right value of either l or A, a trial-and-error method has to be used to check the computed results such that the fraction of residual liquid removed at a particular value of l approaches 1.0 asymptotically when Equation (33) is substituted into Equation (32). The first trial value of l may be a radius of average diameter ($d_p/2$) of a granular particle. Once l and A are determined, then δ could be determined from Equations (30) and (31) for the measured value of R.

Model 2: Blind Side Channel of Varying Cross-Sectional Area. Since the geometry is the wedge-shaped side channel as shown in Figure 2*b* (notice the direction of x axis), one can obtain the relation

$$\frac{R}{1-R} = \frac{a\delta^2}{2l + a(l^2-\delta^2)} \qquad (34)$$

similar to Equation (30) for model 1. From Equation (34) another relation between the length of the side channel and the pore area can be obtained by

$$A = \frac{2R_o A_c \epsilon}{l} \qquad (35)$$

by setting $R = R_o$ at $\delta = l$ into Equation (34). The procedure of determining l or A is the same as described above in the case of model 1. Substitution of Equation (33) into Equation (28) and Equation (35) into Equation (29) results in the expression of "fraction of residual liquid washed out" as a function of washing period or wash volume used for a given solid and liquid system.

WASHING EXPERIMENTS

From the point of view of choosing the wash liquor and the method of analysis of the wash effluent, only two different solids systems and two different residual liquid systems were employed: Solid systems—(1) Noncrystalline solids: Scotchlite glass beads and purified sand; (2) crystalline solids (salt crystals): potassium chloride and copper sulfate. Liquid systems—(1) For residual liquid: (a) Noncolor solution: ethylene glycol, glycerin, saturated solution of potassium chloride; (b) color solution: Dye (ponceau SX) dissolved in glycol and water, respectively (red color), and copper sulfate solution (blue color); (2) for wash liquor: (a) water: for washing noncrystalline solids bed in which glycol, glycerin, or color solution were retained; (b) ethylene glycol: for washing potassium chloride bed in which saturated potassium chloride salt solution (without color) was retained.

Potassium chloride (a U.S. Borax Company product), having a fairly round shape and average particle size of about 1.19 mm. and copper sulfate (a Tennessee Corporation product), having an irregular shape and average particle size of 1.81 mm., were available. These crystals were chosen on the basis of particle size, since most crystals were available only as fine powders or in mixed size ranges. In choosing color material to be dissolved in solvent and to be used as filtrate, one has to consider the possibility of adsorption of color on the solid surface. Most color indicators tried were anionic salts which could be adsorbed on cationic solids, for example, any silicate solid and therefore several cationic disodium salts of organic dye-stuffs were used instead. Ponceau SX, a commercial red dye of Macormick Company, has a very intensive color and is highly soluble in both water and glycol, although less soluble in saturated potassium chloride solutions. Ponceau SX is a disodium salt of 2-(5-sulfo-2, 4-xylylazo)-1-naphthol-4-sulfonic acid. In choosing wash liquor for washing crystals, it was important that the wash liquor should not dissolve the crystals, yet be miscible with the saturated solution of its salt. The choice was dependent of course on the kind of crystals to be washed. Ethyl alcohol was tried for washing potassium chloride crystals, but it caused precipitation from the saturated solution. After many trials with several organic chemicals were made, ethylene glycol was found to work well for washing potassium chloride crystals.

Apparatus and Washing Procedure

The washing apparatus consisted of the wash reservoir, centrifugal pump (3½ gal./min. capacity), by-pass line after pump, wash liquor flow-meter, and the drained bed packed with granular solid as shown in Figure 3. The diameter of the bed was 1¼ in., which gave a value of 0.06 to 0.01 to the particle to bed diameter ratio, depending on the particle sizes used. The height of the bed was about 2½ in.

Wash liquor was allowed to pass through the column from the top after centrifuging, or simply gravity draining was complete and effluent was collected at the bottom of the bed after certain time intervals. In most cases, a small interval (10 sec.) was employed for the first washing period and a larger interval (1 min.) for the later period, because the concentration of the filtrate decreased very rapidly from a larger value to a small value in the initial washing period and then very slowly. During washing the bed was flooded with wash liquor about ¼ in. above the top of the bed. Flow rate was maintained constant during washing. For preparing the crystal beds, a saturated solution of the salt, prepared in advance, was poured through the bed packed with crystals, and then the bed was drained. For preparing the bed in which color solution was supposed to be retained, a known concentration of color solution was prepared very accurately and a calibration curve was constructed for each color solution to relate color intensity to concentration.

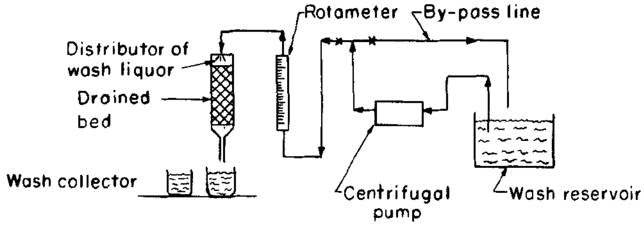

Fig. 3. Washing apparatus.

Analysis of Wash Effluent

The method of analysis was dependent upon the tracer employed. For washing saturated salt solution from the bed of crystals with glycol as wash liquor, water in the wash effluent was determined by the Karl Fischer volumetric titration technique. For washing the colored solution with noncolor solution, a colorimetric method was employed, using a Beckman spectrophotometer.

For washing ethylene glycol from the beds of sand or glass beads with water, the differential refractive index was

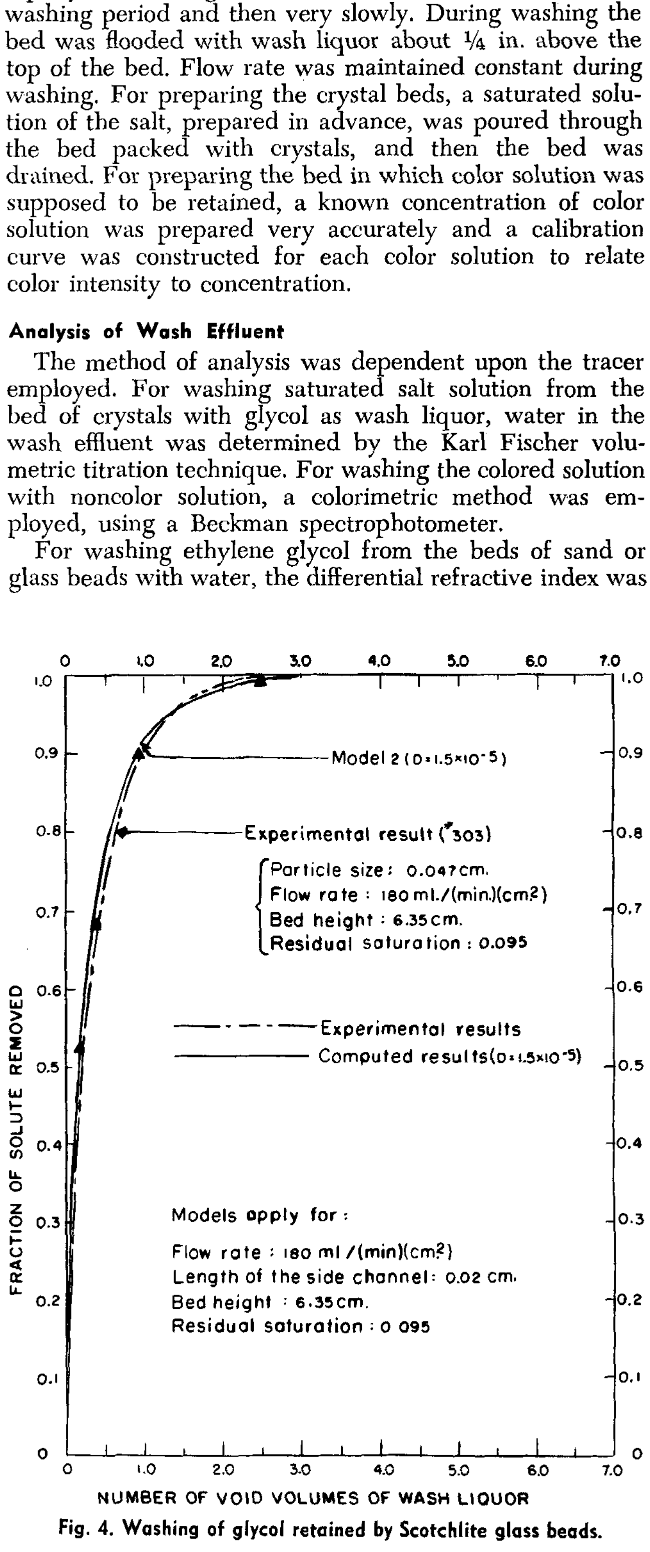

Fig. 4. Washing of glycol retained by Scotchlite glass beads.

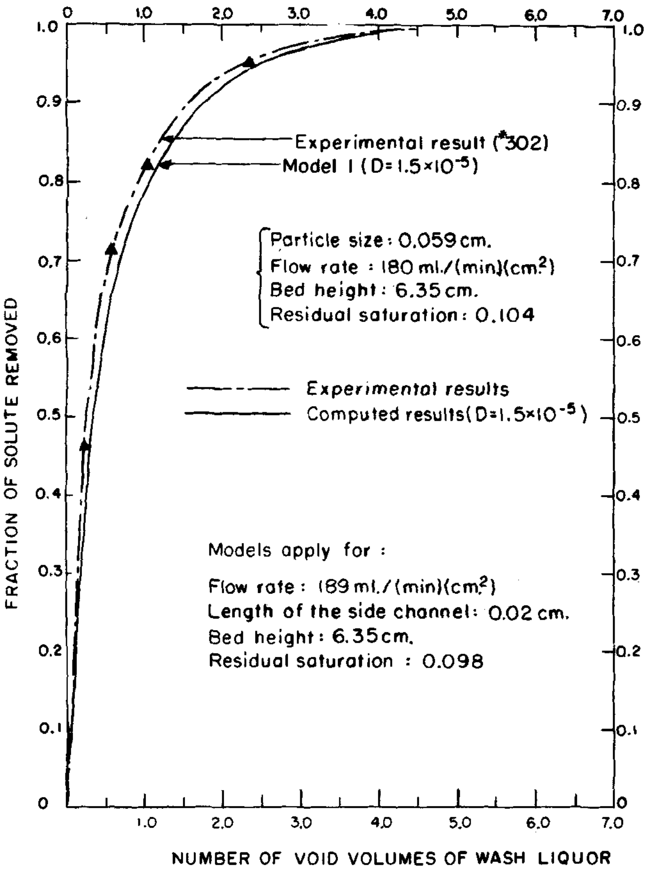

Fig. 5. Washing of glycol retained by purified sand.

measured by a differential refractometer. To determine possible errors arising from the analysis of the wash effluent, the following steps were taken: (1) After washing stopped the cake was broken and leached with a measured amount of the same wash liquor. (2) This solution was analyzed. (3) The material balance on the residual liquid was checked by adding the amount of residual liquid washed out to that retained in the bed after washing stops.

RESULTS AND DISCUSSION

Final results can be plotted in several ways. However, it appears that a plot of the fraction of residual liquid removed vs. number of void volumes of wash liquor may be of most practical interest in characterizing simple filtration and washing. The instantaneous concentration of residual liquid in the wash effluent vs. the washing period would also be of interest if product recovery from the wash liquor is undertaken. The experimental results, Figures 4 through 6, are plotted in terms of the fraction of residual liquid removed vs. number of void volume of wash liquor, and the computed results are plotted on the same sheets for the comparison between the experimental and computed results. Figures 4 and 5 describe the washing performance of the beds of Scotchlite glass beads and of purified sand, both retaining ethylene glycol as residual liquid. Distilled water was used as wash liquor. Figure 6 describes the washing performance of the bed of potassium chloride crystals retaining saturated solution of the salt as the residual liquid. Ethylene glycol was used as wash liquor, which is miscible with saturated solution of potassium chloride but does not dissolve the crystals. Experimental data obtained from the washing of the granular solids are available from reference *11*. For every solid-liquid systems chosen for washing experiment (about twenty runs were made), the results obtained were reproducible within the experimental errors. In general, the same type of fit as shown in Figures 4 and 5 was obtained within the range of variables studied. Details of the range of variables studied and prediction of the theoretical models developed in this study are documented in reference *11*.

The washing model has been applied to beds which have been centrifuged, and thus the residual liquid is presumably present as pendular rings at the particle-particle contact points. In all cases studied, and in all cases of practical interest, the wash liquor is miscible with the residual liquid. Thus, although the washing process has been depicted by the system shown in Figure 7*a*, where diffusion of residual liquid across a stagnant interface is assumed, the actual case may be at least as complicated as depicted in Figure 7*b*, where a moving diffusion boundary is shown, and is probably a great deal more complicated. This assumption has been prompted by the observation (*12*) that the irreducible wetting phase saturation in a porous medium has no measurable effect on the permeability of the medium to an immiscible nonwetting phase. Thus, in all likelihood, the residual liquid is essentially stagnant even in the presence of a flowing stream of miscible wash liquor. This does not eliminate the possibility of some mixing occurring at the interface between the flowing wash liquor and stagnant residual liquid due to buoyancy effects and differences in kinematic viscosities. In spite of these complications, the model used yields a reasonable fit of the data which justifies its use for preliminary engineering design purposes.

In the practical application of the blind channel theory developed in this work, three aspects must be considered. First, does model 1 or model 2 more closely represent the real case? Second, are the side channels completely or only partially full? Finally, what are the best values of the undefined system parameter (primarily l and D) which best represent the experimental data? Figures 4 through 6 illustrate the results of the curve fitting by adjusting these parameters. First, l was assumed to be approximately

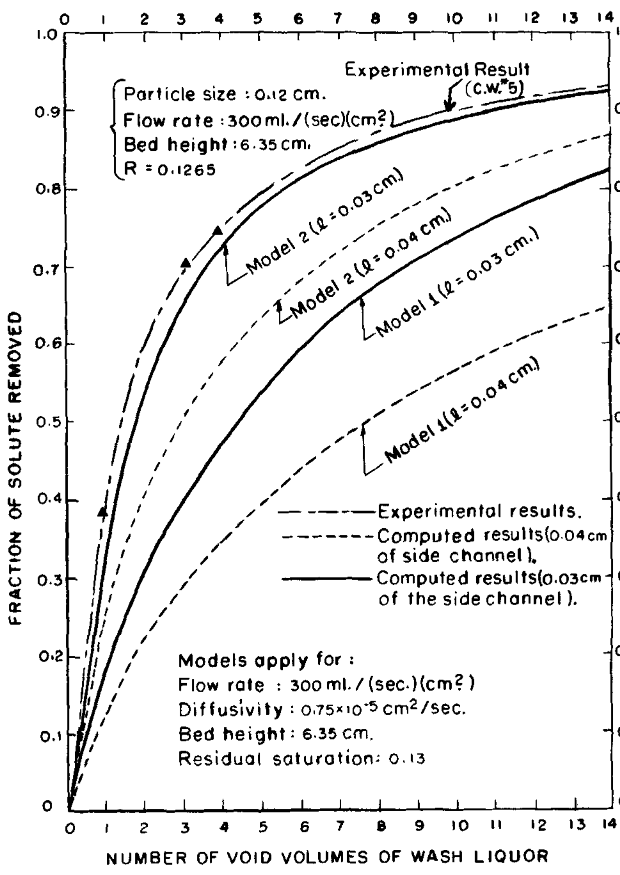

Fig. 6. Washing of saturated solution of potassium chloride retained by its crystal salt.

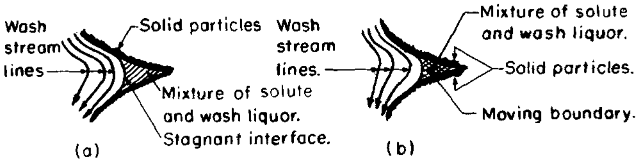

Fig. 7. Flow paths wash liquor and stagnant region of residual liquid.

equal to $d_p/2$. It will be noted that the value of l/d_p used in these trials varied, because the closest results from a standard series of machine computations were chosen. Since washing was performed on beds which had been centrifuged to give an R near the equilibrium ($R_o = 0.09$), δ was assumed to be zero, that is, the side channels were full. This assumption stems from the analogy drawn earlier between R_o and the irreducible wetting phase saturation in two phase fluid flow through porous media. Therefore Equations (33) and (35) were used to determine A for the two models. All other parameters were defined by experimental conditions, except the diffusivity for the residual liquid into the wash liquor and this could be estimated.

The important points to be derived from Figures 4 through 6 are (1) model 2 (wedge shaped channel) seems to fit washing of spherical particles better than model 1 (uniform cross-sectional channel), (2) there is some indication model 1 gives a slightly better representation of the washing of rough or irregularly shaped particles, (3) the fit of the data is quite sensitive to the selection of l, and (4) the fit of the data is less sensitive to the selection of D. Observations 1 and 2 seem reasonable in light of the earlier discussion about the location and configuration of residual liquid in a bed of particles. Observations 3 and 4 are strictly manifestations of the mathematical models. After the best representative model of the experimental data was chosen, the values of the side channel length which led to reasonably good agreement between theory and the washing data were determined. These values are tabulated in Table 1. From these data it can be seen that

$$l \cong 0.38\ d_p \tag{36}$$

over this range of particle sizes. This agrees quite well with a value of 0.33 d_p which comes from assuming that the pendular ring at a contact point between two uniform spheres has a configuration such that the two principal radii of curvature are equal in magnitude and opposite in sign. It must be emphasized that this model for the pendular liquid configuration leads to a curved interface between the residual liquid and wash liquor and the value of $l = 0.33\ d_p$ applies only to the waist of the ring (see Figure 8). More experimental work is required to establish the validity of the partially full side channel models.

A considerable amount of work would be required to make a direct comparison between the present experimental washing data and the washing models of other authors (*1* to *3*). The major difficulty stems from the fact that only the concentration of residual liquid in the wash liquor effluent is considered by these authors. Their time-dependent concentration function must, therefore, be integrated to yield relationships between fractional completion of washing time or wash liquor throughput. Dobie (*3*) assumed that the only mixing of residual liquid with wash liquor was by axial diffusion. He then superimposed axial diffusion (opposite in direction to the wash liquor flow direction) on plug flow of the residual liquid in an initially 100% saturated filter cake. Since axial mixing should be of little consequence in washing of centrifuged beds at the flow rates of interest, a direct comparison with Dobie's model is not warranted. Kuo's (*2*) model assumed that the residual liquid is a stagnant liquid film spread uniformly over the walls for the idealized pores, representing wash liquor flows in plug flow through the central core of these pores. Separate but complete radial mixing within the wash liquor and residual liquid is assumed. The difference in residual liquid concentration in the wash liquor and the stagnant film is assumed to be the driving force for mass transfer. This model is felt to be less realistic than the one used here, and since integration of Kuo's time-dependent concentration function is not a simple matter, direct comparison with the present experimental work has not been attempted.

The only model used for comparison is that of Rhodes (*1*). Although it lacks a fundamental basis, it does offer a simple empirical expression for describing the washing operation. Rhodes' time-dependent concentration function can be written as

$$R = R_o\ c^{-kW} \tag{37}$$

where k is an arbitrary constant having the units of cc. void/cc. wash liquor which relates R to the effluent residual liquid concentration c; for example, $c = kR$, and thus k is a type of mass transfer coefficient. Rhodes' model assumes complete mixing of the residual liquid transferred to the wash liquor within the bed. In order to calculate the fractional completion of washing, the following integration must be performed:

$$F_3 = k \int_0^W e^{-kW} dW = 1 - e^{-kW} \tag{38}$$

Therefore a plot of $\log(1 - F_3)$ vs. W should be a straight line. Figure 9 is a plot of the present washing data according to Equation (38). Included in this figure are the best curves fitted according to the blind side channel models. It can be seen that there is considerable divergence as the washing period progresses. The values of k are tabulated in Table 2. As would be expected, k apparently correlates fairly well with particle size. Since bed height was held constant, the effect of this important variable on k could not be determined. The diffusivity of the residual liquid into wash liquor will also influence k. Even though the blind side channel models are more realistic and provide unique insight into both the retention and washing processes, Equation (38) could be used as an empirical correlation of washing data. If more were known about the influence of d_p on k, this model might also be useful for preliminary design calculation. This blind side channel model clearly gives a better representation

TABLE 1. CORRELATION OF THE LENGTH OF THE SIDE CHANNEL TO THE AVERAGE PARTICLE SIZE

Average particle size d_p, cm.	Length of the side channel, cm.	l/d_p
0.047	0.018	0.383
0.059	0.022	0.373
0.119	0.031	0.382

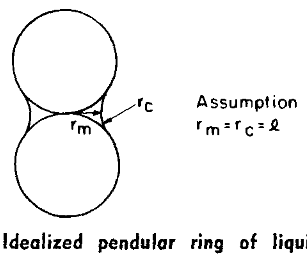

Fig. 8. Idealized pendular ring of liquid at contact point.

TABLE 2. EMPIRICAL VALUE OF CONSTANT k IN RHODES' MODEL WITH THE USE OF PRESENT WASHING DATA

Run No.	Solid	Residual liquid	Wash liquor	Average particle size, cm.	k*
302	Purified sand	Glycol	Water	0.059	0.442
303	Scotchlite glass beads	Glycol	Water	0.047	0.902
C.W. 5	Potassium chloride crystals	Saturated solution of potassium chloride	Ethylene glycol	0.12	0.1645

* k was estimated from the slope of the best straight line with the us of present washing data.

of washing, especially for beds of large particles. It should be pointed out that the models developed here assume a uniform particle size distribution, the perfect shape of the particles, an ideal mode of packaging, etc., although these ideal situations can never exist in practice. Therefore the ratio of the length of the side channel to particle size could be variable, depending upon how close the assumptions made are to real situations.

Finally, it should be pointed out that the model is based on plug flow of the wash liquid through the bed in an axial direction, with the molecular diffusion of residual liquid from side channels into wash liquid as a basic displacement mechanism of miscible liquid-liquid system. However some of the previous studies (*3*, *4*, *9*) assumed that the longitudinal dispersion effects played a predominant role over resistance to mass transfer from residual liquid into the wash liquid. Though no complete experimental data are available at the present time to prove or disprove the relative importance of mass transfer between the residual liquid and wash liquid to longitudinal dispersion effects on overall washing performance, the results obtained in this study appear to predict consistently washing performance as well as the results from previous studies (*9*). It seems, however, to be expected that the rate of mass transfer of residual liquid into the wash liquid flowing through the bed controls the overall washing performance in general.

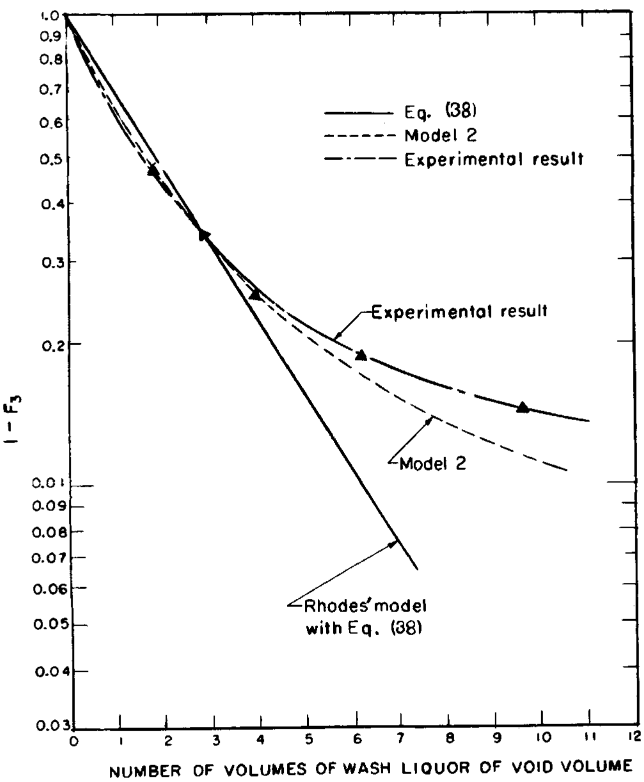

Fig. 9. Washing of potassium chloride crystal bed with glycol; test of Rhodes' model.

CONCLUSIONS

1. A mathematical model of the washing process has been developed on the assumption that the bed is made up of a bundle of parallel capillaries with blind side channels. The wash liquid is assumed to pass in plug flow down through the straight channels with plug flow velocity profile and to displace solute by molecular diffusion from the blind side channels which are full or partially full of residual solution at the start of the washing process. Washing performance computed on the basis of this model with full side channels is shown to agree qualitatively with the experimental washing data on initially centrifuged beds.

2. The analytical study was carried out with two variations of the basic model: straight side channels of constant cross section and tapered or wedge-shaped channels. Agreement with the data was generally better in the case of the second model, although the first served somewhat better for sand beds. The side channels are visualized as being more nearly wedge-shaped for spheres than for the granular sand.

3. The most important unspecified parameter in these models is the length of the side channel l. Fair agreement between the theoretical and experimental results was obtained when $l = 0.38d_p$ for the three systems most thoroughly studied. This agrees remarkably well with the value of $0.33d_p$ that results from calculation based on the pendular ring model for residual liquid in centrifuged beds.

4. Although the blind side channel model gives much better representation of the washing data and is a more satisfactory approximation of the physical process, the integrated form of Rhodes' simple washing model may be useful as an empirical design equation for washing of centrifuged beds of small particles.

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NOTATION

a = area of blind side channel in walls of straight channel per unit volume of straight channel, $(= Av/Q)$ sq.ft./cu.ft.

A = area of blind side channel in walls of straight channel per unit length of straight channel, sq.ft./ft.

A_c = total cross-sectional area of bed, sq.ft.

C = concentration of the filtrate (residual liquid) at y ft. from the top of the straight channel and x ft. from the entrance of the blind channel at time t, lb./cu.ft. of filtrate (mixture of solute and wash liquor)

C_o = weight of residual liquid retained initially/volume of residual liquid, lb./cu.ft.
D = molecular diffusivity between the filtrate and wash, sq.ft./min.
d_p = diameter of sphere having same volume as particle constituting the porous medium, ft.
F = fraction of residual liquid washed
I_o = second kind of zero order of the modified Bessel function
I_1 = second kind of first order of the modified Bessel function
k = constant in Equation (41)
l = length of a side channel, ft.
N = rate of transport of filtrate from the blind side channels into wash liquor flowing down the straight channel, lb./(min.)(sq.ft.), of blind side channel cross section
Q = flow rate of wash, cu.ft./min.
R = residual saturation defined as volume of residual liquid per void volume, cu.ft./cu.ft.
s = dummy variable in Equation (31)
t = washing period, min.
v = average velocity of the fluid based on the cross-sectional area of void spaces, ft./min.
V = total volume of the bed, cu.ft.
W = volume of wash liquor throughput/volume of void volume
y = height of packed column, ft.
Y = aDy/v

Greek Letters

$\mu(t, y)$ = concentration of filtrate in the straight channel at time t and y ft. from the top of straight channel, lb. of filtrate/cu.ft. of liquids (mixture of filtrate and wash)
$\rho(\theta, y)$ = concentration of filtrate in the straight channel
ϵ = porosity, volume of voids per total volume of bed, cu.ft./cu.ft.
δ = length of the side channel unfilled with the residual liquid, ft.
$\theta = t - y/v$ = the time at which filtrate is moved from the side channel, min.
β_n = roots of J_o

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Flow of Viscoelastic Fluids Through Porous Media

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Local volume averaging of the equations of continuity and of motion over a porous medium is discussed. For steady state flow such that inertial effects can be neglected, a resistance transformation is introduced which in part transforms the local average velocity vector into the local force per unit volume which the fluid exerts on the pore walls. It is suggested that for a randomly deposited, although perhaps layered, porous structure this resistance transformation is invertible, symmetric, and positive-definite. Finally, for an isotropic porous structure (the proper values of the resistance transformation are all equal and are termed the resistance coefficient) and an incompressible fluid, the functional dependence of the resistance coefficient is discussed with the Buckingham-Pi theorem used for an Ellis model fluid, a power model fluid, a Newtonian fluid, and a Noll simple fluid. Based on the discussion of the Noll simple fluid, a suggestion is made for the correlation and extrapolation of experimental data for a single viscoelastic fluid in a set of geometrically similar porous structures.

Darcy's law, involving a parameter k, termed the *permeability*, was originally proposed as a correlation of experimental data for the flow of an incompressible Newtonian fluid of viscosity μ moving axially with a volume flow rate Q through a cylindrical packed bed of cross section A and length l under the influence of a pressure difference ΔP (*1*, p. 634):

$$\frac{\Delta P}{l} = \frac{\mu}{k} \frac{Q}{A} \quad (1)$$

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Equation (1) has suggested for an isotropic porous medium a vector form of Darcy's law (*1*, p. 634):

$$\nabla P + \frac{\mu}{k} \mathbf{V} = 0 \quad (2)$$

A major difficulty of this equation has been that since it was not derived, the average pressure P and average velocity $\mathbf{V}$ were undefined. Whitaker (*2*) has recently derived a generalization of Equation (2) appropriate to an anisotropic porous medium by taking a local average of the equation of motion. In his result, P and $\mathbf{V}$ are