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Analysis of Relationships Between Permeability, Pressure on the Solids, and Porosity for Calcium Carbonate

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Abstract

This study aims to evaluate the constitutive equations for pressure on the solids and permeability of porous media consisting of calcium carbonates with different degrees of polydispersity. The constitutive relations are intended to assist in the modeling and simulation of sedimentation operations when theory of mixtures of continuum mechanics is used. In this work, a porous media was obtained after the complete sedimentation of aqueous suspensions of calcium carbonate. The gamma-ray attenuation technique was used, which allowed the realization of measurements of the distribution of porosity in the sediment before and after liquid percolation. The experimental results showed a considerable degree of compressibility for calcium carbonates, and significant deviations from the Kozeny-Carman correlation when the carbonates were used to express permeability. Therefore, the use of the incompressibility hypothesis for this solid in equations that model sedimentation may not be a viable consideration. Overall, this study provides relevant information about sedimentation for situations in which the formation of compressible sediments occurs.

Keywords: constitutive equations, permeability, porosity, pressure on the solids, sedimentation

1. Introduction

The sedimentation phenomenon has a great importance in several processes related to the chemical and mining industry. For this reason, the behavior of particles settling in a fluid has been widely studied over the years in both Newtonian fluids [1–6] and non-Newtonian fluids [7–13].
The first study to evaluate the sedimentation theoretically was proposed by Kynch [14]. In the Kynch model, the descending interface is not described mathematically, being necessary to obtain it empirically. The upward interface is provided by way of lines (or curves) of equi-concentration. Thus, the theory only describes the propagation of waves of the same concentration that propagates from the bottom of the base to the clarified interface. Four distinct regions are verified during the sedimentation process according to Kynch’s theory (Figure 1):

Several studies in the literature mention that Kynch’s model describes reasonably well the sedimentation that forms sediments with a low degree of compressibility, such as non-flocculated mineral particles [15]. For situations where solid-fluid separation causes the formation of compressible sediments, the theory is not indicated to describe sedimentation.

The accommodation of the solid materials is related to the existing forces on the particles that are not taken into account in the mathematical modeling developed by Kynch [14].

In order to describe the phenomenon in a way that is closer to reality, it is verified that the modeling developed by Kynch has been modified. Thus, the equation of the motion (associated with the force balance of the particle) has been included into the modeling of the
sedimentation phenomenon \cite{5-7, 16}. An example of modeling that includes the balance of particle forces is the theory of mixtures of continuum mechanics.

The theory of mixtures of continuum mechanics has been used successfully in describing solid-fluid separation systems. Such theory has been indicated even in situations where the formation of compressible porous media occurs (as it usually occurs in sedimentation and filtration operations) \cite{5, 6}.

The application of theory of mixtures of continuum mechanics is confronted with the difficulty in obtaining the constitutive equation of pressure on the solids, $P(\varepsilon_s)$, and permeability of porous media, $k(\varepsilon_s)$. Generally, constitutive equations are empirically determined and express the relationships between porosity, pressure on the solids, and permeability of the porous matrixes.

The functions, $P(\varepsilon_s)$ and $k(\varepsilon_s)$, when used in the mathematical modeling of the phenomenon, associate the compression effects to the porous medium, representing the thickening and filtration processes in a more reliable way with the physical reality \cite{17–20}.

Despite the importance and the several techniques available in the literature for determination of constitutive equations, many works adopt the porous media as incompressible like simplifying assumption, and the minority solve numerically the problem of thickening and filtration with the formation of compressible porous media \cite{18}.

In this context, this study aims to evaluate the relationships between porosity, permeability, and stresses in solids, $P(\varepsilon_s)$ and $k(\varepsilon_s)$, for porous media composed of carbonates. The methodology used in this study (gamma-ray attenuation technique) avoids using compression-permeability cells through densification presses, reaching reliable results for $P(\varepsilon_s)$ and $k(\varepsilon_s)$ even at low pressures.

Moreover, the permeability results, $k(\varepsilon_s)$, determined experimentally were compared with the values estimated by the classical Kozeny-Carman correlation for porous media with different degrees of size and polydispersity.

\section{Theoretical analysis}

In the theory of mixtures of continuum mechanics, the equations of continuity and motion for each constituent of the mixture must be used. For the case of one-dimensional flow through the porous media, the numbers of scalar available equations to study the problem are two continuity (Eqs. (1) and (2)) and two motion equations (Eqs. (3) and (4)):

\begin{align}
\frac{\partial (p_f \varepsilon_f)}{\partial t} + \nabla \cdot (p_f \varepsilon_f v_f) &= 0. \quad (1) \\
\frac{\partial (p_s \varepsilon_s)}{\partial t} + \nabla \cdot (p_s \varepsilon_s v_s) &= 0. \quad (2)
\end{align}
\[
\rho_f \varepsilon_f \left[\frac{\partial v_f}{\partial t} + (\nabla v_f) v_f\right] = \nabla \cdot T_f - m + \rho_f \varepsilon f \quad (3)
\]
\[
\rho_s \varepsilon_s \left[\frac{\partial v_s}{\partial t} + (\nabla v_s) v_s\right] = \nabla \cdot T_s - m + \left(\rho_s - \rho_f\right) \varepsilon_s g. \quad (4)
\]

where \( \varepsilon_f \) is the local porosity of the suspension; \( \varepsilon_s \) is the local volumetric concentration of solids; \( \rho_f \) and \( \rho_s \) are, respectively, the fluid and solid densities; \( v_s \) and \( v_f \) are, respectively, the interstitial velocities of the solid and fluid; \( m \) represents the resistive force that the fluid exerts on the solid matrix; \( g \) is the local gravity; and \( T_f \) and \( T_s \) are, respectively, the stresses exerted on the fluid phase and on the solid phase.

From the analysis of Eqs. (1)–(4), it can be seen that the number of variables to be measured are seven (two concentrations, two velocities, two stresses, and a resistive force). Thus, another three equations are required to nullify the number of degrees of freedom and making system of equations solvable.

Considering that the sum of the volume fraction of solids and fluid is equivalent to 1 (\( \varepsilon_s + \varepsilon_f = 1 \)), then it is necessary to determine only two constitutive equations to make the system of equations solvable: one for stress in solids (\( T_s \)) and other for the resistive force.

### 2.1. Stress on the solids

For the resolution of the system, it is necessary to adopt constitutive hypotheses related to the tension on the solid (\( T_s \)) and for the resistive force (\( m \)).

d’Ávila [21] developed a constitutive theory considering the solid-fluid system as an isotropic medium. The authors indicate that the stress tensor may be represented as follows:

\[
T_i = -p_i I - T''_i \quad (5)
\]

where \( p_i \) and \( T''_i \) are, respectively, the pressure (the arbitrary tensor) and the extra stress (constitutive part of the tensor). The term \( T''_i \) represents the dynamic part of the stress tensor, and the term \( p_i I \) is the static part, being \( I \) the identity tensor.

The majority of studies in the literature suggest the dependence of pressure on the solids as an exclusive function of the porosity of the system:

\[
T_i(\varepsilon_f) = -P(\varepsilon_f) I. \quad (6)
\]

An example of such expressions can be enunciated by the model proposed by Arouca [6]:

\[
P(\varepsilon_s) = a \varepsilon_s^b \quad (7)
\]

where \( a \) and \( b \) are model parameters.
2.2. The resistive force

The representation of the resistive force vector is another necessary condition to make determined the system formed by the equations of continuity and motion for the solid and the fluid. For the case of one-dimensional slow flow in porous media, the resistive force can be represented by Darcy’s law:

\[
m = \frac{\mu \epsilon_f}{k(\epsilon_f)} (v_s - v_f)
\]

where \( k \) is the permeability of the porous medium and \( \mu \) is the viscosity of the fluid.

There are models in the literature that describe the relationship between permeability and porosity from the empirical determination of its parameters. An example of such expressions can be enunciated the model proposed by Tiller and Leu [22]:

\[
k(\epsilon_s) = k_0 \left( \frac{\epsilon_s}{\epsilon_{sc}} \right)^{\eta}
\]

where \( k_0, \epsilon_{sc}, \) and \( \eta \) are parameters of the model.

The correlations in literature that express the permeability as a function of porosity allows obtaining constitutive equation \( k(\epsilon_s) \) without the experimental determination. An example of such correlation is the Kozeny-Carman (Eq. (10)). Such correlations allow correlating the permeability with the properties of the particles and the porosity of the medium:

\[
k = \frac{(D_p \varphi) \epsilon_f^2}{180(1 - \epsilon_f)^2}
\]

where \( \varphi \) is the sphericity of the particle and \( d_p \) is the diameter of the sphere of the same volume of the particle.

Endo et al. [23] proposed an equation that relates the porosity with the permeability, contemplating the effects of form, and polydispersity of the particulate material:

However the use of the equation of Endo et al. [23] requires particle sizes to follow the log-normal distribution. In addition, there is in some cases a certain difficulty to estimate some of the parameter of equation-like factor form. For this reason, it is often necessary to empirically obtain the relationships between permeability and porosity.

The experimental determination of constitutive equations, \( k(\epsilon_s) \) and \( P(\epsilon_s) \), that govern dimensional percolation fluids through porous media with low porosity can be made with the aid of compression-permeability cells through presses densification tests [24, 25].

However, according Tiller et al. [26], the use of compression-permeability cells at low stresses may lead to considerable errors in the characterization of porous media. According to the authors, the porosity distribution in the porous matrix as homogeneous must be considered.
as simplifying assumption. This situation is not achieved when performing tests at low pressures, because the uniformity of concentration in the sample is not achieved.

Furthermore, the lowest stress applied in porous medium by a compression-permeability cell is often above the tension in which the filter cake and the sediments are submitted in filtration and thickening operation.

In this context, Damasceno [5] developed a methodology that has been successfully used by some studies in the literature [17–20] to assess the relationships between porosity, stress in solids, and permeability of porous media. This technique was used in this study and avoids using compression-permeability cells through densification presses, reaching reliable results at low pressures.

3. Material and methods

In this study, samples of calcium carbonate (designed as calcium carbonate A and calcium carbonate B) were used as suspended particles in aqueous continuous phase.

The granulometric analyses of the materials (calcium carbonate A and calcium carbonate B) were obtained using the particle size analyzer Malvern Mastersizer Microplus MAF 5001®. Figure 1 represents the cumulative distribution obtained for the carbonates used in this study.

As can be seen in Figure 2, the samples of calcium carbonate B have a larger range of particle size distribution, that is, such material can be considered more polydisperse than calcium carbonate A.

In Table 1, the volumetric particle diameters corresponding to 10% ($D_{0.1}$), 50% ($D_{0.5}$) and 90% ($D_{0.9}$) of the cumulative distribution (diameter cutting) along with the Sauter mean diameter ($D_{3,2}$) are shown.

The density of solids was determined by helium pycnometry. The results are shown in Table 2.

3.1. Experimental methodology

The methodology proposed Damasceno [5] to determine the relationship between porosity, stress in solids, and permeability can be established from the following considerations and simplifying assumptions:

a. The flow through the porous medium is slow and steady one dimensional (z direction).

b. Darcy’s law represents the resistive force.

c. Tension in solids is an exclusive function of local porosity.

d. The terms of the inertial equation of motion for the constituent solid are negligible.

Under these conditions, the equations of continuity for the fluid and the solid phase (Eqs. (1) and (2)) and the equation of motion for the solid (Eq. (4)) reduce to
\[
\frac{d}{dz}(\epsilon_x \nu_x) = 0 \\
\frac{d}{dz}(\epsilon_y \alpha_y) = 0
\] (11) (12)

Figure 2. Cumulative distribution of the material solids.

<table>
<thead>
<tr>
<th>Solid</th>
<th>(D_{0.1}) ((\mu m))</th>
<th>(D_{0.5}) ((\mu m))</th>
<th>(D_{0.9}) ((\mu m))</th>
<th>(D_{3.2}) ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate A</td>
<td>5.39</td>
<td>20.48</td>
<td>48.80</td>
<td>12.84</td>
</tr>
<tr>
<td>Calcium carbonate B</td>
<td>12.11</td>
<td>48.73</td>
<td>134.71</td>
<td>29.73</td>
</tr>
</tbody>
</table>

Table 1. Volumetric particle diameters.

<table>
<thead>
<tr>
<th>Solid</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate A</td>
<td>2.84</td>
</tr>
<tr>
<td>Calcium carbonate B</td>
<td>2.81</td>
</tr>
</tbody>
</table>

Table 2. Density of calcium carbonate.
\[ \frac{dP_s}{dz} = \frac{\mu \varepsilon_f}{k(\varepsilon_f)} (v_f - v_s) + \left( \rho_s - \rho_f \right) \varepsilon_s g \]  

(13)

Integrating Eqs. (11) and (12) takes the relationships shown below:

\[ \varepsilon_s v_s = q_s \]  

(14)

\[ \varepsilon_f v_f = q_f \]  

(15)

Substituting Eqs. (14) and (15) in (13):

\[ \frac{dP_s(\varepsilon_f)}{dz} = \frac{\mu \varepsilon_f}{k(\varepsilon_f)} \left( \frac{q_f}{\varepsilon_f} - \frac{q_s}{\varepsilon_s} \right) + \left( \rho_s - \rho_f \right) \varepsilon_s g \]  

(16)

The functions \( P_s(\varepsilon_s) \) and \( k(\varepsilon_s) \) are, respectively, called constitutive equations for pressure on the solids and permeability of porous media.

The experimental determination of constitutive equations for \( P_s(\varepsilon_s) \) and \( k(\varepsilon_s) \) can be done by using Eq. (16) and by establishing at least two different situations of the concentration distribution in the sediment and the superficial velocity of the solid \( (q_s) \) and the liquid \( (q_f) \) [5–7].

The first experiment can be idealized in a static porous media, in which the superficial velocity of solid and liquid is null \( (q_f = q_s = 0) \). For this condition, and with the motion equation for the solid constituent, the expression that relates the stress in solids and porosity of the porous media is given by

\[ P_s = \left( \rho_s - \rho_f \right) g \int_0^L \varepsilon_s dz \]  

(17)

where “z” is the axis reference measured from the top of the sediment height “L.”

By establishing the function \( P(\varepsilon_s) \), a second experiment can be designed to determine the permeability of the porous media. The sediment formed inside the test tube undergoes an accommodation process, which was characterized for a new configuration of the porous matrix, resulting from the slow liquid percolation through the porous media. With such conditions, Eq. (16) can be rewritten as

\[ k = \frac{\mu q_f}{\frac{dP_s}{dz}} = \frac{\mu q_f}{\left( \rho_s - \rho_f \right) \varepsilon_s g} \]  

(18)

In this study, the characterization of a static porous media was obtained after the complete sedimentation of aqueous suspensions of calcium carbonate. For this, the system was allowed to stand for 48 hours to stabilize the porous matrix. Then, the flow control valve was opened, and the sediment obtained a new particle accommodation due to the percolation of the liquid in the system.
A porous sintered copper plate was used to prevent the passage of solids and to promote the percolation of the liquid, which resulted in the new stability condition. With the concentration profile established along the height of the column before and after percolation of the liquid, the stress in solids and permeability of the porous medium were determined, from Eqs. (17) and (18). The volumetric concentration of the suspension at the beginning of the tests was $\varepsilon_{s0} = 12\%$.

3.2. The gamma-ray attenuation technique

The use of nondestructive techniques for the analysis of porous media is a very reliable alternative when simple sampling cannot be used as it interferes in the configuration and stability of the system. In this study the concentration profile in the sediment was determined based on the count of radiation pulses emitted by the radioisotope americium-241.

The technique used is based on the number of photons reaching the radiation detector scintillation. The radiation is converted into electrical pulses which are then amplified and quantified. The experimental system used to determine the solid concentration was composed of a source of gamma rays, collimators, radiation detection equipment, a test tube in which the suspension of the solid under study was placed, and a device to promote the vertical displacement of the test tube, enabling to study the sedimentation process in several positions (Figure 3).

![Figure 3. Experimental apparatus.](http://dx.doi.org/10.5772/intechopen.72913)

The variation of the intensity of a collimated beam of monoenergetic gamma rays passing through a physical medium can be determined by the equation of Lambert. For the particular case where the mean that focuses the radiation is suspended and solid-liquid state as a reference solution without suspended solids, this equation takes the following form [27]:

\[
\text{Intensity} = I_0 e^{-\mu x}
\]
\[
\ln \left( \frac{I}{I_0} \right) = \beta \varepsilon_s
\]  

(19)

where \( I \) is the intensity of the beam after passing through the physical medium and \( I_0 \) is the intensity of beam passing through a reference condition.

The intensity of the beam after passage through the physical medium must be corrected by the time resolution of the system or dead time from the following equation:

\[
R = \frac{I}{1 - \tau I}
\]  

(20)

in which \( R \) is the corrected counting from the number of pulses that pass through the physical medium and \( \tau \) is the resolution time of the system. Thus, Eq. (19) becomes

\[
\ln \left( \frac{R_0}{R} \right) = \beta \varepsilon_s
\]  

(21)

being the corrected counting \( R_0 \) the number of pulses of radiation passing through the measuring cylinder (without solids concentration).

The application of Eq. (21) is made from calibration tests to estimate the parameter \( \beta \). Identifying the local solid concentration using the gamma-ray attenuation technique was possible by determining the specific calibration curve for the solids for each particular suspension of calcium carbonate.

4. Results

Obtaining the distribution of solid concentration in the sediment before to percolation of liquid, it was possible using Eq. (16) to determine the pressure on the solids as function of solid concentration (Figure 4).

Analyzing Figure 4, it can be observed that the carbonates presented variation in the porosity at different pressures, indicating, in this way, a considerable degree of compressibility. Thus, the use of the incompressibility hypothesis for carbonates in equations that model sedimentation may not be a viable consideration.

Moreover, the results showed that the calcium carbonate B was more compressible than calcium carbonate A. This fact can be explained because particulate materials with a higher degree of polydispersity when subjected to a given pressure deform more easily due to smaller particles that accommodate themselves in the interstices of the larger particles.

In Figure 4, the curve representing the function, \( P(\varepsilon_s) \), was adjusted by estimating the parameters of Eq. (7). The estimated parameters of the model (a, b) are shown in Table 3.
There is an absence in the literature of expressions that allow expressing the relationship between the pressure on the solids and porosity, without the necessity of empirical determination. For this reason, the gamma-ray attenuation technique appears as a viable alternative, especially in situations where the use of denser presses is not indicated, i.e., low pressures.

### 4.1. Determination of constitutive equation for permeability of porous medium

Obtaining the solid concentration profile in the sediment before and after the percolation of liquid, it was possible with Eq. (17) to determine the permeability of the porous medium as function volumetric concentration of solids (Figure 5).

In Figure 5, it is observed that the decrease in porosity results in the reduction in permeability of the porous matrix. The permeability may be understood as a measure of the facility of a

**Table 3. Parameters of the model for pressure on the solids.**

<table>
<thead>
<tr>
<th>Solid</th>
<th>$a$ (Pa)</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate A</td>
<td>$2.20 \times 10^6$</td>
<td>10.79</td>
</tr>
<tr>
<td>Calcium carbonate B</td>
<td>$4.12 \times 10^6$</td>
<td>12.37</td>
</tr>
</tbody>
</table>

Figure 4. Pressure on the solids as a function of the solid concentration in the sediment.

Figure 5. Porosity ($\phi$) as a function of pressure on the solids ($P_s$) for calcium carbonate A and B.
flowing fluid in a medium. Therefore, with the reduction of the volume of voids (smaller porosity), the reduction in the permeability of the medium occurs.

As can also be seen in Figure 5, the results showed that calcium carbonate A had the permeability-porosity curve below the calcium carbonate B. This can be explained because particulate materials, which have smaller sizes, form porous media less permeable.

In Figure 5 the curve representing the function $k(\varepsilon_s)$ was adjusted by the classical model proposed by Tiller and Leu [22]:

$$k(\varepsilon_s) = k_0 \left(\frac{\varepsilon_s}{\varepsilon_{sc}}\right)^{-\eta}$$  \hspace{1cm} (22)

The estimated parameters of the model ($k_0$, $\varepsilon_{sc}$ and $\eta$) are shown in Table 4:

The experimental results shown in Figure 5 were compared with the values estimated by the Kozeny-Carman correlation (Figure 6).

As can be observed in Figure 6, the experimental values and the estimated values by Kozeny-Carman correlation showed that the reduction in particle size resulted in a decrease in the permeability curve.

It can also be seen in Figure 6 that the theoretical results predicted by the Kozeny-Carman correlation underestimated the experimental values for both studied carbonates.
This difference verified in Figure 6 can be explained because the Kozeny-Carman correlation was proposed based in monodisperse materials and therefore includes only the effects of size and shape.

As the Kozeny-Carman correlation does not contemplate the polydispersion effects; it can be considered that this parameter increased the experimental values of the permeability-porosity relationship, causing the observed deviations.

5. Conclusions

In this study, the theory of mixtures of continuum mechanics was described as an interesting alternative for the theoretical description of sedimentation. The constitutive equations for pressure on the solids and for permeability of porous media that constitute the system of mathematical equations were determined experimentally for carbonates.

<table>
<thead>
<tr>
<th>Solid</th>
<th>$k_0$ $(\text{cm}^2)$</th>
<th>$\varepsilon_s$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonate A</td>
<td>7.28.10^{-9}</td>
<td>0.08</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcium carbonate B</td>
<td>8.50.10^{-9}</td>
<td>0.09</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4. Parameters of the tiller and Leu [5] model.

Figure 6. Comparison between the experimentally results with the values estimated by the Kozeny-Carman correlation.

This difference verified in Figure 6 can be explained because the Kozeny-Carman correlation was proposed based in monodisperse materials and therefore includes only the effects of size and shape.

As the Kozeny-Carman correlation does not contemplate the polydispersion effects; it can be considered that this parameter increased the experimental values of the permeability-porosity relationship, causing the observed deviations.

5. Conclusions

In this study, the theory of mixtures of continuum mechanics was described as an interesting alternative for the theoretical description of sedimentation. The constitutive equations for pressure on the solids and for permeability of porous media that constitute the system of mathematical equations were determined experimentally for carbonates.
The gamma-ray attenuation technique using americium-241 proved to be satisfactory to determine the porosity of porous media composed of carbonate, as well as to determine the relationships of pressure on the solids and permeability.

The increase of the carbonate size distribution range caused the increase of the compressibility of the porous medium, indicating in this way a relation between the polydispersity of the particulate material and the compressibility of the porous matrices.

The theoretical values predicted by the Kozeny-Carman correlation for the relationships between permeability and porosity underestimated the experimental values. The deviations were quite significant for both studied carbonates, demonstrating that such correlation should be used with careful for polydisperse materials.

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