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THE EFFECT OF CHEMICAL REACTIONS ON THE TRANSPORT PROPERTIES OF POROUS MEDIA

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SUMMARY – Research on modeling the effects of chemical reactions on flow in porous media, mainly arising from geochemical and geothermal applications, is reviewed. The review highlights the methods used in modeling the effects of reactions on porosity and then summarizes some of the main relations used in modeling the associated permeability changes.

1. INTRODUCTION

Chemical reactions in porous media occur in a wide range of industrial and scientific applications including: storage of heat generating materials (coal, char, sawdust, haystacks, oil containing natural products and radioactive waste), packed-bed catalytic chemical reactors, petroleum and geothermal reservoirs, bulk storage of foodstuffs (e.g. grain, potatoes and onions) and many more.
In this paper we will review some of the past work on porosity and permeability changes resulting from chemical reactions. Firstly we will consider how porosity is linked to chemical reactions and then we will review and compare some of the main approaches for representing the dependence of permeability on porosity. In the context of geochemical science, the methods for modeling geochemical reactions have developed rapidly since the early **1960's** (Bethke, **1996).** Computer modeling has played a revolutionary role in helping geochemists to use quantitative models to understand topics such as analysis of sediments and hydrothermal alteration, ore deposits, migration of contaminants from mine tailings and toxic waste sites and scaling in geothermal wells.

2. TRANSPORT PROPERTIES OF POROUS MEDIA

To study the flow in a typical porous medium (heterogeneous, non-uniform and anisotropic) we need to consider the macroscopic properties. These properties are; porosity (ϕ), permeability (k) and tortuosity (τ) (Greenkorn, 1983). Permeability is the single most important transport property since it is directly related to the flow velocity through Darcy's law.

Early studies relating porosity-permeability changes during fluid flow in reactive porous media are rare and scattered throughout various disciplines. The field has developed significantly in the past ten years. However, the methods used depend on the field of study and the application and general procedures are not available.

The main difficulty is that a simple relationship between permeability and porosity cannot adequately represent the physical behaviour of fluid flow in a porous medium (Baumgartner *et. al.*, **1997).** The structure of the porous medium should be incorporated by considering, for example: the statistics of pore geometry (Phillips, **1991),** pore space geometry (Pruess, **1997)** or pore structure (Pape *et. al.*, 2000). However, in practice porosity is the property which is most easily measured and permeability/porosity relationships are the most practically useful. Most of the empirical approaches are exponential or power-low relationships and the calculated permeabilities may vary widely (from **3** to **10** times) for porosities larger than **10%**(Pape *et. al.*, 2000).

3. CHANGES IN POROSITY DUE TO CHEMICAL REACTION

Chemical reactions can be mathematically modeled through chemical kinetics, local equilibrium or a combination of both (Steefel *et al.*, **1994;** Steefel *et al.*, **1996;** Lichtner, **1996).** In general terms, for a homogeneous porous **medium,** changes in porosity due to chemical reactions in mineral components can be calculated without difficulty (Pape *et. al.*, **2000)** by using the formula:

$$\phi = 1 - X - Y \qquad (1)$$

where ϕ is the porosity of the medium, X and Y are the volume fraction of soluble and insoluble minerals respectively. The difficulty of course is in the calculation of X. Several approaches are found in literature for relating porosity to the reaction.

3.1 Continuum model

The volume fraction of soluble minerals can be written as:

$$X = \sum_{m=1}^{M_{\min}} \phi_m \qquad (2)$$

where ϕ_m is the volume fraction for mineral m and $M_{\min}$ is the total number of soluble minerals. For each mineral the deposition equation can be written in the form.

$$\frac{\partial \phi_m}{\partial t} = \frac{R_m}{\rho_m} \tag{3}$$

where ρ_m is the mineral density and R_m is the deposition/precipitation rate (Lichtner, 1996).

3.2 Spherical grain model

Another somehow similar approach was proposed by Chadam *et al.*, (1996). They assumed that the solid minerals consist of uniformly distributed spherical grains. Thus:

$$X = \sum_{m=1}^{M_{\min}} \frac{4}{3}\pi \eta_m r_m^3 \tag{4}$$

where η_m is the grain number density of solid mineral m and r_m is the grain radii. Then the deposition equation takes the form:

$$\frac{\partial r_m}{\partial t} = \frac{R_m}{4\pi r_m^2 \rho_m \eta_m} \tag{5}$$

3 3 Cubic (angular) grains model

Ortoleva P. *et. al.*, (1987) and Chadam *et al.*, (1996) used a more general porosity-reaction relation with a local average volume for the grain of L_m^3 (i.e. cubic grains or the so-called angular grains). In this case:

$$X = \sum_{m=1}^{M_{\min}} \eta_m L_m^3 \tag{6}$$

and

$$\frac{\partial L_m^3}{\partial t} = \frac{R_m}{\rho_m \eta_m} \tag{7}$$

Normally all the minerals are considered to be totally soluble, ie. $Y = 0$. However, for insoluble minerals Y=constant in the continuum model, while for the spherical and cubical granular models (respectively):

$$Y = \sum_{n=1}^{N_{\min}} \frac{4}{3}\pi \eta_n r_n^3 \quad \text{and} \quad Y = \sum_{n=1}^{N_{\min}} \eta_n L_n^3$$

where n is the insoluble mineral, and $N_{\min}$ is the total number of insoluble minerals, having constant dimensions r and L.

All the above expressions correspond to the total porosity (Lichtner, 1996) which may differ from the real connected porosity used in the transport equations. They neglect the effects of compaction and dilation in the porous media (Steefel *et al.*, 1994).

Most researchers have used the continuum approach, **(2)** and (3), for handling the changes in porosity associated with multi-mineral reactions (Steefel *et. al.*, 1994; Lichtner, 1996; Pape *et. al.*, 2000). However, several other customized expressions have been used for calculating porosity change in terms of the **amount** of mineral deposition (Verma and Pruess, 1988; Olivella *et. al.*, 1996; Pruess, 1997; Sutopo and Arihara 1999).

4. CHANGES IN PERMEABILITY DUE TO CHEMICAL REACTION

There are several formulae for calculating the change of permeability associated with chemical reactions. Most of them are based on a combination of theoretical and empirical relations and express permeability as a function of grain dimensions or porosity. Several forms of the formulae are variations of the Kozeny relationship (Takeno *et. al.*, **2000**). However, these relations do not account for such local effects as pore clogging and very little experimental data is available to justify the use of one from the other (Lichtner, 1996). Some of these relationships are listed below.

4.1 Empirical formulae

Lerman, (1979), Domenico et. *al.* (1990), and Oelkers, (1996), (references for **(8)–(15)** are included in these volumes) summarized some of the empirical approaches relating permeability to grain size or porosity. These relations are purely empirical and were determined mainly from experimental permeability determinations for sedimentary rocks (sand, gravel and clay). The units for **k** are Darcies unless stated otherwise

(i) Hazen, relationship for loose sand

$$k = \left(\frac{v_f}{g}\right) C\, d_{10}^2 \tag{8}$$

Where d_{10} is effective grain size *(cm)* defined as the value where 10% of the particles are finer and 90% coarser, C is a constant varying, from 100 to 150 (cm/s), v_f is fluid kinematic viscosity and g is the gravitational acceleration.

(ii) Harleman, used another formula of similar form to (8):

$$k = (6.54\times10^{-8})\, d_{10}^2 \tag{9}$$

(iii) Krumbein and **Monk**, used the formula:

$$k = 760\, d^2\, e^{-1.31\varsigma} \tag{10}$$

where **d** is the geometric mean diameter in (*mm*) and ς is the log standard deviation of the grain size distribution.

(iv) Bloch, equation

$$Log.k = \bar{c}_1 + \bar{c}_2\bar{d} + \bar{c}_3\tilde{s}^{-1} + \bar{c}_4\tilde{r} \qquad (11)$$

Where $\bar{c}_1$, $\bar{c}_2$, $\bar{c}_3$ and $\bar{c}_4$ are designated constants, $\bar{d}$ is the average grain diameter, $\tilde{s}$ is the Trask sorting coefficient, and $\tilde{r}$ is the rigid grain constant.

(v) **Bethke, used,** for well stored clastic deposits:

$$Log\ \mathrm{k} = C\phi + \mathrm{D} \qquad (12)$$

where C and D are coefficients obtained from laboratory measurements of core porosity and permeability.

(vi) Krumbein and Monk, used:

$$\mathrm{k} = 2.47\times10^{-19}\, r^2 \qquad (13)$$

For sands with grain radius, $0.005 < r < 0.1$ cm.

(vii) Bryant, for marine clayey sediments used:

$$k = 10^{-9}\left(\frac{\phi}{1-\phi}\right)^7 \qquad (14)$$

(viii) Robertson, for aragonitic sediment, $0.2 < \phi < 0.7$, used:

$$k = 7.25\times10^{-11}\left(\frac{\phi}{1-\phi}\right)^7 \qquad (15)$$

The same data were also matched to an equation of the form: $\log k = -17.0 + 13.6\phi$, (Lerman, **1979).**

(xi) Nutting, **(1930),** (as cited by, Bear, **1972)** proposed:

$$\mathrm{k} = 0.617\times10^{-11}\, d_{10}^2 \qquad (16)$$

where k (in cm^2 or approximately 10^8 darcy) and d_{10} (in *microns*).

(x) Weir and White, **(1996),** derived an empirical relationship for permeability changes resulting from surface deposition and early dissolution in an initial rhombohedral array of uniform spheres, which was **used** by Sutopo and Arihara, **(1999),** for modeling silica deposition in injection wells.

$$k = k_\circ\left(1-\left(1-\left(\frac{\phi-\phi_c}{\phi_\circ-\phi_c}\right)^{1.58}\right)^{0.46}\right) \qquad (17)$$

where ϕ_c is the critical porosity at which permeability reduces to zero ($\phi_c = \mathbf{0.2}$ for Silica).

Many other relations can be found in Nelson, **(1994).**

4.2 Porosity dependent permeability

Many theoretical models of permeability vs porosity are based on the Hagen-Poiseuille solution for the average laminar flow velocity through a bundle of circular tubes. This leads to what is often called the Kozeny equation.

$$k = \frac{\phi^3}{(1-\phi)^2}\frac{1}{S_V^2\, c_K} \qquad (18)$$

where c_K is the Kozeny constant and S_V is the specific surface area (total particle surface/volume of the particle), which can be defined in terms of the mean particle diameter (spherical) **d, as** $S_V = 6/d_p$. The Kozeny equation **has** experienced many modifications for different applications (Ergun, **1952;** Bird *et. al.*, **1960;** Camp, **1964;** Greenkom, **1983;** Kaviany, **1991;** Oelkers, **1996).**

(i) Carman-Kozeny equation ($c_K = 5$) for flow in packed beds (Kaviany, **1991).**

$$k = \frac{\phi^3}{(1-\phi)^2}\frac{d_p^2}{180} \qquad (19)$$

(ii) Blake-Kozeny equation ($c_K = 25/6$) for flow in packed columns (Bird *et. al.*, **1960).**

$$k = \frac{\phi^3}{(1-\phi)^2}\frac{d_p^2}{150} \qquad (20)$$

(iii) Ergun equation for highly turbulent flow ($\mathrm{Re} < 1000$) of gases in packed beds (Bird *et. al.*, **1960).**

$$k = \frac{\phi^3 d_p^2}{150(1-\phi)^2} + \frac{\nu_f\, \phi^3 d_p}{1.75(1-\phi)\mathrm{v}} \qquad (21)$$

where ν_f is the kinematic viscosity of fluid and **v** is the magnitude of the fluid velocity.

(iv) Kozeny-Stein equation for clogging process around grains e.g. in sand filters (Camp, **1964).**

$$k = k_\circ\left[\frac{(1-\phi_\circ)^2}{(1-\phi_\circ+\sigma)^2}\frac{(\phi_\circ-\sigma)^3}{\phi_\circ^3}.\right.$$

$$\left\{\sqrt{\frac{\sigma}{3(1-\phi_\circ)}+\frac{1}{4}}+\frac{\sigma}{3(1-\phi_\circ)}+\frac{1}{2}\right\}\Bigg] \tag{22}$$

where $k_,$, $\phi_\circ$ are the initial permeability and porosity respectively and σ is the deposition ratio (Camp, **1964).**

(v) White, **(1995), used** the following equation, also derived from Carman-Kozeny equation **(19),** for the dissolution and precipitation of polymorphic silica.

$$k = k_\circ\left(\frac{\phi}{\phi_\circ}\right)^3 \tag{23}$$

(vi) McCume *et al.,* **(1979)** used a normalised version of the Blake-Kozeny equation **(20)** for modeling permeability changes in acidized oil and gas wells (limestone and sandstone). Olivella *et. al.,* **(1996)** used the same equation for the porosity-permeability changes in unsaturated salt rocks.

$$k = k_\circ\left(\frac{\phi}{\phi_\circ}\right)^3\left(\frac{1-\phi_\circ}{1-\phi}\right)^2 \tag{24}$$

(vii) Lichtner, **(1996)** used a model similar to **(24),** which he called a 'phenomenological power law' for representing the permeability dependence on porosity in a mixture of K-feldspar, gibbsite, kaolinite and muscovite.

$$k = k_\circ\left(\frac{\phi}{\phi_\circ}\right)^3\left[\frac{1.001-\phi_\circ^2}{1.001-\phi^2}\right] \tag{25}$$

(viii) Schechter *et. al.,* (1969), developed a model based on change in pore size distribution from surface reaction of dilute hydrochloric acid on limestone when acidizing oil wells.

$$k = k_\circ\left[\frac{\phi}{\phi_\circ}\right]^2 \exp[2(\phi-\phi_\circ)] \tag{26}$$

(ix) Itoi *et. al.,* **(1987),** used the Kozeny-Stein equation **(22)** for modeling the permeability drop associated with silica precipitation in the vicinity of injection wells. Using $\sigma = \phi_\circ - \phi$, he wrote **(22)** in the form:

$$k = k_\circ\left[\left(\frac{\phi}{\phi_\circ}\right)^3\left(\frac{1-\phi_\circ}{1-\phi}\right)^2\right.$$

$$\left.\left\{\sqrt{\frac{\phi_\circ-\phi}{3.(1-\phi_\circ)}+\frac{1}{4}}+\frac{\phi_\circ-\phi}{3.(1-\phi_\circ)}+\frac{1}{2}\right\}\right] \tag{27}$$

This model is really a modified version of **(24).**

(x) Pape *et. al.,* **(1999),** proposed a third order polynomial in porosity. It is based on a fractal model of pore-space and the Carman-Kozeny equation.

$$k = A@ + B\phi^2 + C(10\phi)^{10} \tag{28}$$

where **A,** B and C are calibrating coefficients. It was applied to large data sets from clean and shaly sandstone and pure shales. This model was implemented in the SHEMAT simulator for single-phase (liquid) water-rock interaction in sedimentary basins (Pape *et. al.,* **2000).**

(xi) Ortoleva *et. al.,* **(1987)** and Wei and Ortoleva, **(1990), used** the Fair-Hatch equation (Bear, **1972).** It was developed from the Carman-Kozeny equation and some dimensional considerations of granular media using both spherical and cubical porosity models of **(4)** or **(6).** This equation was also verified experimentally (Bear, **1972).**

(xii) Verma and Pruess, **(1988),** assumed a system of nonintersecting flow channels with either circular tubular or planar cross sections to derive formulae for permeability as a function of porosity, channel dimensions and critical porosity. These algorithms have been incorporated into the TOUGH2 geothermal simulator (Battistelli *et. al.,* **1997;** Sutopo and Arihara, **1999).**

Several other models of permeability dependence on either porosity or grain size can be found in Lerman, **(1979).**

It is possible to compare the models given in equations **(23-27)** since they all define permeability as a function of porosity. For low values initial porosity ($\phi_\circ = 0.1$ in Figure **1)** the difference between the models is insignificant for $\phi < \phi_\circ$ (deposition) except for the Schechter *et. al.,* **(1969),** model. For $\phi > \phi_\circ$ (dissolution) the permeability increases exponentially for Lichtner, **(1996),** and McCume *et. al.,* **(1979),** while it increases only linearly in Schechter *et. al.,* **(1969),** White, **(1995),** and Itoi *et. al.,* **(1987).** For the high initial porosity $\phi_\circ = 0.5$ **of** Figure **2,** the difference between models during deposition $\phi < \phi_\circ$ is still relatively small while for dissolution only the Lichtner, **(1996), and** McCume *et. al.,* **(1979),** models behave reasonably ($k \rightarrow \infty$ as $\phi \rightarrow 1$). Generally the Lichtner, **(1996),** model seems to give the best match for both regions $\phi < \phi_\circ$ and $\phi > \phi_\circ$. The Itoi *et. al.,* **(1987)** model fails to cover the whole range of porosity values because of the occurence of a negative root as porosity increases. The model is intended deposition and for pore clogging only. The Weir and White, **(1996)** model on the other hand seems to behave reasonably for $\phi_\circ > \phi > \phi_c$ (precipitation **only.** It cannot be compared completely with the other models because of the use of a cut-off or critical porosity value at which the permeability goes to zero.

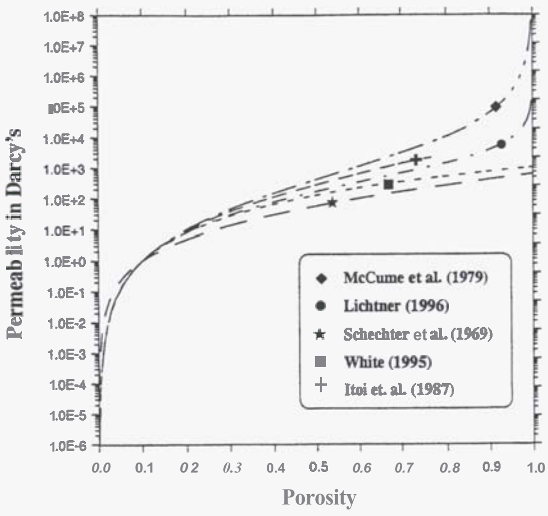

Figure 1 Comparison between equations (23), (24), (25), (26), and (27) for $k_{\circ} = 1$ Darcy and $\phi_{\circ} = 0.1$

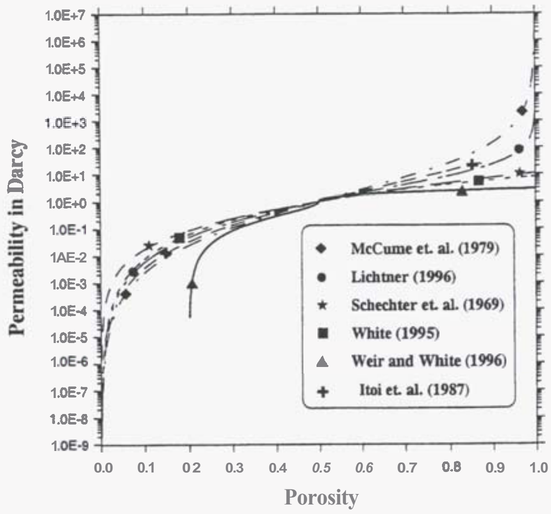

Figure 2 Comparison between equations (23), (24), (25), (26), (27) and (17) for $k_{\circ} = 1$ Darcy, $\phi_{\circ} = 0.5$ and $\phi_c = 0.2$ in equation (17)

5. REACTION SURFACE AREA

The catalytic nature of porous media provides the reactants with a huge contact area thus increasing the rate of reaction. For example the surface area of the available rock is a key property governing silica precipitation in geothermal reservoirs (Itoi *et. al.,* 1987; White and Mroczek, 1998). The effect is complicated when the surface area changes with the dissolution or precipitation of minerals. Several relationships for the dependence of area on porosity have been suggested.

(i) Itoi *et. al.,* (1987), used the Carman-Kozeny equation to calculate the surface area in terms of permeability. Using $A = (1-\phi_{\circ})\, S_V$ (19) becomes:

$$A = \left(\frac{\phi_{\circ}^3}{5.k}\right)^{1/2} \tag{29}$$

Then permeability is evaluated in terms of porosity using (27).

(ii) Several other models used a general porosity-dependent surface area of the form:

$$A = A_{\circ}\left(\frac{\phi}{\phi_{\circ}}\right)^n \tag{30}$$

White, (1995), and Takeno *et al.,* (2000) used $(n = 1/2)$, while Lichtner, (1996), used $(n = 2/3)$.

(iii) Another model proposed by White and Mroczek, (1998) specifically for quartz, was incorporated with a specific empirical rate equation.

6. CONCLUSIONS

The review presented above clearly demonstrates the lack of a universal relationship between porosity and permeability. Therefore in modeling permeability-porosity changes resulting from chemical reactions it is advisable to use an adaptable code that can use any relationship for reaction-porosity, surface area- porosity and permeability-porosity.

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