

# A Model for Intergranular Pressure Solution Creep, Thermo-mechanical-chemical Coupling

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## Abstract

Assessment of intergranular pressure solution (IPS) creep has substantial safety and economic importance in reservoirs for hydrocarbon production, geothermal operations, underground CO<sub>2</sub> sequestration, and hydrogen storage processes. IPS creep is a temperature-dependent, stress-driven deformation mechanism that alters mineral grain shapes by dissolution, precipitation, and diffusion in a chemically closed system. The mechanical compaction and chemical reactions of minerals lead to dissolution or precipitation related to alterations in porosity and permeability that impact the flow and, ultimately, the lifetime of the reservoir. IPS creep can be examined with experiments and some thermodynamic analytical solutions. The IPS creep equations for uniaxial compaction are mainly derived based on the linear kinetic relations between chemical dissolution and precipitation rates. According to the theory, the mineral grains have spherical shapes arranged in a cubic-packed form. Similar models also estimate the compaction occurred at slightly greater porosities. These models frequently overestimate compaction and strain rates by up to many orders of magnitude when the porosity is below 0.2. The reason is that the reaction rate parameters are estimated based on empirical equations in which the saturation indices of minerals are assumed constant. Moreover, the rate of change of grain diameters is set constant. A better approximation can be achieved using the thermodynamic databases and iterative time-dependent kinetic calculations that can be carried out in a geochemical computation program such as PHREEQC. The comparison results are consistent with experimental measurements. The proposed algorithm, mainly combining the conventional IPS equation with geochemical computation, is helpful for better inspection purposes.

## 1. Introduction

The flow and operational lifetime of the reservoir are eventually impacted by changes in porosity and permeability caused by the compaction of minerals and their chemical reactions. Evaluation of the intergranular pressure solution (IPS) creep to predict the impact of the mineral compaction mechanism is economically and operationally crucial for reservoirs (Barbot, 2022; Viswanathan et al., 2022).

Spiers et al. (2004) proposed theoretical IPS creep equations for uniaxial compaction and assumed linear kinetic relations between chemical dissolution and precipitation rates. According to the theory, the mineral grains have spherical shapes arranged in a cubic-packed form.

Similar models also estimate compaction at slightly greater porosities (Malvoisin & Baumgartner, 2021). These models are typically convenient solutions, but they frequently overestimate compaction and strain rates by up to many orders of magnitude when the porosity is below 0.2 or even higher. The reason is that the reaction rate parameters are estimated based on empirical equations in which the saturation indices of minerals are assumed constant. Moreover, the rate of change of grain diameters is set constant. Van den Ende et al. (2019) developed an improved thermodynamic IPS model by introducing an upscaled equation to capture the physics at lower porosity.

This study suggests a straightforward algorithm that integrates PHREEQC (Parkhurst & Appelo 2013) with the traditional IPS equation to improve the inspection of stress-driven deformation of rocks.

## 2. Methodology

Implementing IPS idealizes the minerals as a regular arrangement of spheres in a cubic-packed form, meaning that a single spherical grain is in contact with identical neighbors. It is presumed that this grain is made up of an isotropic, pure solid mineral that dissolves in the pore fluid, or there is precipitation on the surface (Lehner 1995).

Examine a single intergranular contact, as shown in Fig. 1, between two spherical grains of diameter  $d$  that are the same, and the minerals are soluble in aqueous pore fluid. The spherical minerals are assumed to be in chemical equilibrium with the pore fluid at constant pressure and temperature. The minerals dissolve or reprecipitate as the stress is applied while deforming and compacting.

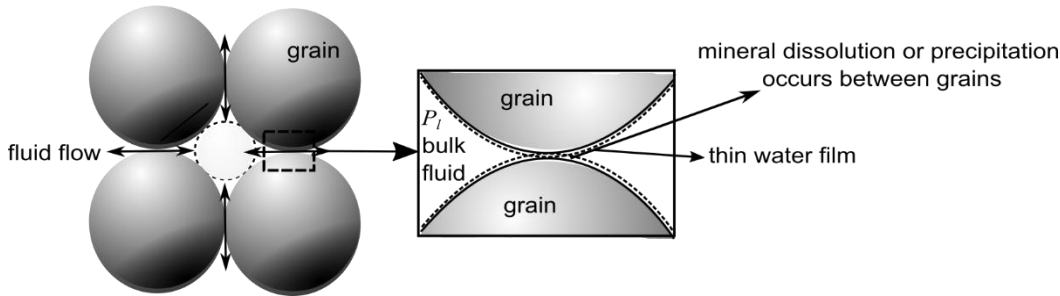


Fig. 1: Schematic illustration of stressed cubic-packed spherical grains containing a pore fluid solution phase at pressure.

During the measurements the porosity change is estimated based on the instantaneous length of the sample  $l$ , the radius of the pressure vessel  $\zeta$ , and the volume of the solid sample  $V_s$  as  $\phi = (\pi\zeta^2 l - V_s)/(\pi\zeta^2 l)$ . The volumetric strain can be expressed as  $e_v = (\phi_0 - \phi)/(1 - \phi)$ , and the volumetric strain rate is estimated respect to the shorting rate of the sample  $\dot{\epsilon} = \dot{l}/l$ , where  $\dot{l} = -dl/dt$ .

### 2.1 Existing IPS model

The typical IPS model contains three volumetric strain rate equations constituting major mechanisms: dissolution  $\dot{\epsilon}_{dis}$ , precipitation  $\dot{\epsilon}_{pre}$ , and diffusion  $\dot{\epsilon}_D$ . The overall total strain rate  $\dot{\epsilon}_T$  is obtained with the sum of these three equations as given below (Spiers et al., 2004; Zhang et al., 2010):

$$\dot{\epsilon}_T = \dot{\epsilon}_{dis} + \dot{\epsilon}_D + \dot{\epsilon}_{pre} \quad (1)$$

The volumetric strain rate for each rate-controlling process for dissolution, diffusion, and precipitation can be subsequently calculated as follows:

$$\dot{\epsilon}_{dis} = R_{dis} \frac{\left[ \exp\left(\frac{\beta\sigma_e\Phi}{RT}\right) - 1 \right] \frac{f_{dis}(\phi_0, e_v)}{6}}{d (1 - e_v)^{1/3}} \quad (2)$$

for diffusion:

$$\dot{\epsilon}_D = DCS \frac{\left[ \exp\left(\frac{\beta\sigma_e\Phi}{RT}\right) - 1 \right]}{d^3} \frac{\overbrace{f_D(\phi_0, e_v)}}{144\pi d^2} \frac{1}{(1-e_v)^{1/3}} \quad (3)$$

for precipitation:

$$\dot{\epsilon}_{pre} = R_{pre} \frac{\left[ \exp\left(\frac{\beta\sigma_e\Phi}{RT}\right) - 1 \right]}{d} \frac{\overbrace{f_{pr}(\phi_0, e_v)}}{A_c} \frac{6}{A_p (1-e_v)^{1/3}} \quad (4)$$

where  $R_{dis}$  and  $R_{pre}$  are the dissolution and precipitation velocities,  $d$  is the grain diameter,  $\sigma_e$  is the applied stress,  $\Phi$  is the molar volume of the mineral,  $\beta$  is the strain-dependent parameter, and  $e_v$  is the volumetric strain.  $f_{dis}$ ,  $f_D$  and  $f_{pre}$  stand for the porosity functions related to the strain.

In equation 3,  $D$  is the molecular diffusion coefficient,  $C$  is the concentration of the mineral, and  $S$  is the thin water film thickness at the grain boundary.

The pore area in the cubic-packed grain geometry changes as the grains are compacted under stress.  $A_p$  can be estimated as:

$$A_p = 4\pi r^2 - 6[2\pi r(r - \chi)] \quad (5)$$

where  $r$  is the radius of the grain and  $\chi$  is the central distance from the spherical grain to the neighbor spherical grain that can be estimated depending on the volumetric strain as:

$$\chi = r(1-e_v)^{1/3} \quad (6)$$

The strain-dependent parameter  $\beta$  related to the contact area of per unit grain  $A_c$  is calculated as follows:

$$\beta = \frac{6d^2(1-e_v)^{2/3}}{A_c} \quad (7)$$

The contact area  $A_c$  is:

$$A_c = 6\pi(r^2 - \chi^2) \quad (8)$$

The rate of change in grain radius is estimated with a cubic equation:

$$-2r^3 + 4.5r^2\chi - 1.5\chi - r = 0 \quad (9)$$

## 2.1 Improved IPS model coupled with iPHREEQC

Instead of coupling the major deformation mechanisms separately, the total strain rate  $\dot{\epsilon}_T$  can be obtained from a single equation as given below:

$$\dot{\epsilon}_X = R_{dp} \frac{\left[ \exp\left(\frac{\beta\sigma_e\Phi}{RT}\right) - 1 \right]}{d} \phi_t(t) \quad (10)$$

$R_{dp}$  is the kinetic dissolution/precipitation velocity,  $\phi_t(t)$  is the rate of change of porosity calculated based on the rate of change of the grain radius.

$$R_{dp} = \frac{C_m}{A_r} \Phi \quad (11)$$

$C_m$  is the moles of a kinetic reactant that reacted in the current time step in mol s<sup>-1</sup> obtained from iPHREEQC, and  $A_r$  is the total reactive surface area of the mineral estimated as (Noiriel et al., 2009):

$$A_r = A_0 \left( \frac{m_0}{m_i} \right)^{2/3} \quad (12)$$

$m_i$  is the mineral concentration that changes over time and is computed in iPHREEQC,  $m_0$  the initial mineral concentration. The rate of change in porosity  $\phi_t(t)$  is estimated depending on the molar change of minerals. To estimate the initial reaction surface area  $A_0$  of calcite,

$$\phi_t(t) = \phi_0 - \left( 1 - \frac{m_0}{m_i} \right) \quad (13)$$

The diameter change of a spherical grain can be approximated with the following relation:

$$\delta = \frac{\left( 1 - \frac{A_0}{A_r} \right)}{\xi} \quad (14)$$

where  $\xi$  the ratio between total volume over one-grain sphere volume.

The following kinetic rate equation, taking into account the temperature dependence, describes the dissolution or precipitation process of minerals (Palandri & Kharaka, 2004):

$$R_{mi} = \omega_{mi} k_{i25} \exp\left(\frac{-E_{i-a0}}{R_{gas}} \left[ \frac{1}{T} - \frac{1}{298.15} \right]\right) \left| 1 - \Omega_i^p \right|^q \quad (15)$$

in which the subscript  $i$  denotes the  $i^{\text{th}}$  mineral,  $k_{i25}$  is the kinetic rate constant at 25 °C,  $\omega_{mi}$  is the specific surface area of the total pore space,  $E_a$  is the activation energy, and  $\Omega$  is the saturation index.

The exponents  $p$  and  $q$  are empirical constants related to the precipitation, and dissolution (Lasaga 1984).

The overall process is iteratively computed concerning kinetic rates law in the interface of iPHREEQC coupled with MATLAB. The critical parameters computed in geochemical modeling are the  $C_m$ , the moles of calcite that reacted in the current time step, and  $m_i$ , the rate of change in moles of the calcite.

### 3. Comparison of IPS theory

A comparison is carried out between the conventional IPS model and the proposed equation coupled with iPHREEQC above with the experimental study of Zhang et al. (2010), who conducted experiments on uniaxial compaction on wet calcite powders made from pure calcite to assess rate-controlling process and ascertain whether creep occurs by intergranular pressure solution (IPS) under these conditions. The calculations are carried out with strain measurements obtained from a uniaxial compaction experiment for a wet sample and empirically determined chemical kinetic rates. The tests were conducted with pre-saturated  $\text{CaCO}_3$  solution as the pore fluid at  $150^\circ\text{C}$ , with effective stresses of 30 MPa. Four samples are considered for the comparison, and the size of the sample grains varied from 12 to 82  $\mu\text{m}$ , as shown in Table 1. Each experiment is carried out with six grams of calcite saturated in pure water. The initial porosity of samples is around 0.3.

Tab. 1. Grain diameters of calcite samples (Zhang et al., 2010).

Sample	Grain diameter ( $\mu\text{m}$ )
M1	$37\pm 8$
M8	$82\pm 8$
M9	$22\pm 8$
M11	$12\pm 4$

According to Zhang et al. (2010), sample temperature measurements were raised from  $25^\circ\text{C}$  to  $150^\circ\text{C}$  for approximately twelve hours during the tests. However, a complete thermal and chemical equilibrium was believed to be established in twenty hours.

#### 3.1 Existing IPS model parameters

The kinetic parameters that were used to calculate the strain rates with the existing IPS model are provided in Table 2.

Tab. 2. Mechanical and chemical kinetic parameters used for existing IPS model. All values were taken from Zhang et al. (2010).

parameters	Values at $150^\circ\text{C}$
Dissolution velocity, $R_{dis}$	$8.49\times 10^{-10}$ ( $\text{m s}^{-1}$ )
Precipitation velocity, $R_{pre}$	$3.81\times 10^{-9}$ ( $\text{m s}^{-1}$ )
Diffusion coefficient $D$	$5.98\times 10^{-10}$ ( $\text{m}^2 \text{s}^{-1}$ )
Water film thickness $S$	$1\times 10^{-9}$ (m)
Applied Effective stress $\sigma_e$	$30\times 10^6$ (Pa)
Molar volume of calcite $\Phi$	$3.62\times 10^{-5}$ ( $\text{m}^3 \text{mol}^{-1}$ )

In equation 3, the  $C$  is estimated based on the solubility product  $K_{sp} \sim C^2$ , according to Zhang et al. (2010). The solubility product of calcite mineral is empirically calculated as  $\log(K_{sp}) = -171.9065 - 0.077993T + 2839.319/T + 71.595.\log(T)$ .

### 3.2 Improved IPS model parameters

The main difference between the conventional IPS and the improved equation is related to the geochemical computation. The geometric assumptions have been used to calculate the reaction surface area and the volume of each experiment. The area calculation is based on the experiments of Zhang et al. (2010) with six grams of calcite, which means 0.06 initial moles of calcite exist in an experiment. First, it is assumed that the total volume of a sample is a sphere and calculated as  $2.172 \times 10^{-6} \text{ m}^3$  based on the molar volume of calcite. Then, the initial radius of the total sphere becomes  $r = 0.008 \text{ m}$ . The total surface area of that sphere is  $8.042 \times 10^{-4} \text{ m}^2$ . The kinetic rate constant and the activation energy of calcite are  $1.2 \times 10^{-6} \text{ mol m}^2 \text{ s}^{-1}$  and  $23.5 \text{ KJ mol}^{-1}$ , respectively, assigned in iPHREEQC calculations (Palandri & Kharaka, 2004).

### 4. Results

The proposed new method is compared with the existing IPS model; the volumetric strain measurements are obtained from Zhang et al. (2010) to calculate the strain rates of each sample with four different grain diameters. As can be seen in Fig. 2b, the conventional IPS calculation results (i.e., solid lines) overestimate the strain rate compared to the measurements, whereas the novel method coupled with PHREEQC provides more consistent outcomes. The root mean square logarithmic error (RMSLE) between Eq. 1 results and Eq. 10 evaluations varies around 1.4 to 1.5. The dynamically computed saturation index of calcite mineral in a batch system via iPHREEQC using the LLNL thermodynamic database gives more accurate results. The dynamic computation of the molar changes of calcite and its kinetic rate altering at each step due to changes in the reaction surface area significantly impacts the results. As the volumetric strain increases over time, calcite dissolution hinders the strain rate, whereas the conventional IPS theory fails to predict at larger strain. The slight deviation between the novel equation results (i.e., dashed lines) and the measurements may be due to the fact that we consider the entire amount of calcite assumed in the new model as a monolithic sphere affecting the reaction surface area. Note that this monolithic sphere assumption is only for evaluating geochemical reactions, not for the deformation.

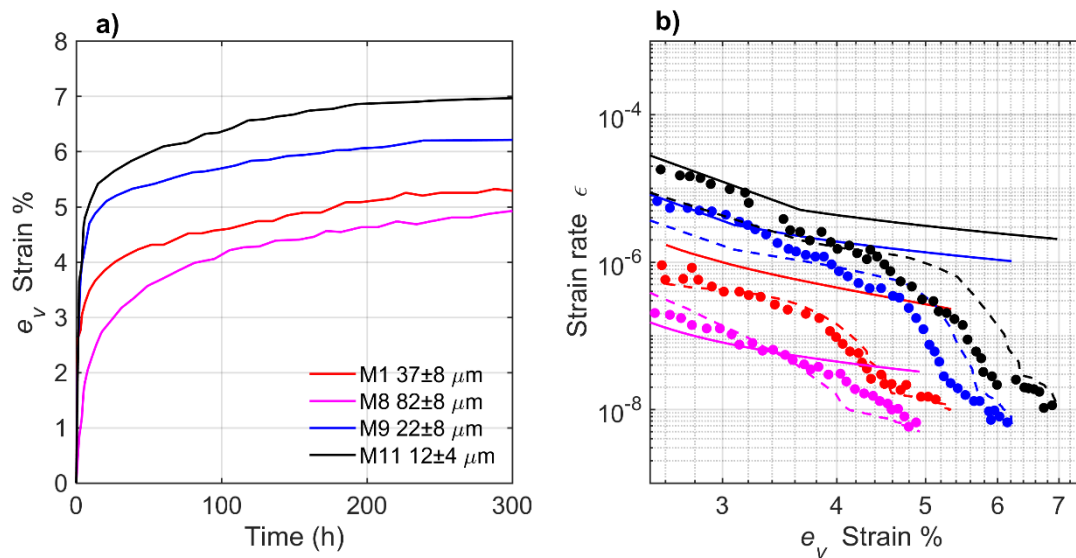


Fig. 2: a) Strain over time obtained from Zhang et al. (2010). b) Strain rate comparison between the conventional IPS equation Eq. 1 (solid-lines), measurements (solid-markers), and Eq. 10 coupled with iPHREEQC (dashed-lines). Applied effective pressure  $\sigma_e = 30 \text{ MPa}$ .

At the start of the test, sample M11, which has the smallest grain diameter, produces the highest strain rate. Nevertheless, the strain rate abruptly drops as the volumetric strain rises to 5%. The strain rate behaves proportionately concerning grain diameter; however, the most significant drop in strain rates occurs at the smallest grain diameters when the volumetric strain surpasses 4%. The minerals become less compacted as the grain diameter increases, as the behavior of M8 can be seen.

## 5. Conclusion

This study discusses the drawbacks of the conventional IPS theory and elaborates on an alternative set of equations for the IPS theory that has been proposed and examined. The conventional IPS models often overestimate strain rates and compaction by several orders of magnitude. The reason is that the saturation indices of minerals are assumed to be constant in empirical equations that are used to estimate the reaction rate parameters. Additionally, the rate at which grain diameters change is fixed. Instead of using constant parameters, thermodynamic databases, and iterative time-dependent kinetic reaction rate calculations provide a more accurate approximation. The algorithm can be modified and applied to more complex heterogeneous fluid-rock interaction systems that can be handled in MATLAB coupled with the iPHREEQC.

## Sources

BARBOT, S.: A Rate-, State-, and Temperature-Dependent friction law with competing healing mechanisms, *Journal of Geophysical Research: Solid Earth*, 127(11), (2022).

<https://doi.org/10.1029/2022JB025106>

CROIZÉ, D., BJØRLYKKE, K., JAHREN, J., & RENARD, F.: Experimental mechanical and chemical compaction of carbonate sand. *Journal of Geophysical Research: Solid Earth*, 115, (2010). B11204.

<https://10.1130/10.1029/2010JB007697>

LASAGA, A. C.: Chemical kinetics of water-rock interactions. *Journal of Geophysical Research: Solid Earth*, 89(B6), (1984), 4009–4025. <https://doi.org/10.1029/JB089iB06p04009>

LEHNER F.K.: A model for intergranular pressure solution in open systems. *Tectonophysics*, 245(3-4), (1995), 153–170. [https://10.1130/10.1016/0040-1951\(94\)00232-X](https://10.1130/10.1016/0040-1951(94)00232-X)

MALVOISIN, B., & BAUMGARTNER, L. P.: Mineral Dissolution and Precipitation Under Stress: Model Formulation and Application to Metamorphic Reactions. *Geochemistry, Geophysics, Geosystems*, 22(5), (2021). <https://doi.org/10.1029/2021GC009633>

NOIRIEL, C., LUQUOT, L., MADÉ, B., RAIMBAULT, L., GOUZE, P., & VAN DER LEE, J.: Changes in reactive surface area during limestone dissolution: an experimental and modelling study, *Chemical Geology*, 265, (2009), 160–170. <https://doi.org/10.1016/j.chemgeo.2009.01.032>.

PALANDRI, J. L., & KHARAKA, Y. K.: A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling: USGS Report 2004-1068. U.S. Geological Survey, (2004).

PARKHURST, D. L. & APPELO, C. A. J.: Description of input and examples for PHREEQC version 3 a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Techniques and Methods. Amsterdam, Netherlands, (2013). <https://pubs.usgs.gov/tm/06/a43/>

SPIERS, C. J., DE MEER, S., NIEMEIJER, A. R., & ZHANG, X.: Kinetics of rock deformation by pressure solution and the role of thin aqueous films. In S. Nakashima, *Physicochemistry of Thin Film Mater.* 129–158, Tokyo: Universal Academy Press, (2004).

VAN DEN ENDE, M. P. A., NIEMEIJER, A. R., & SPIERS, C. J. : Influence of grain boundary structural evolution on pressure solution creep rates. *Journal of Geophysical Research: Solid Earth*, 124, (2019), 10210–10230. <https://10.1130/10.1029/2019JB017500>

VAN NOORT, R., SPIERS, C. J., & PENNOCK, G. M.: Compaction of granular quartz under hydrothermal conditions: Controlling mechanisms and grain boundary processes. *Journal of Geophysical Research: Solid Earth*, 113, (2008) B12206. <https://10.1130/10.1029/2008JB005815>

VISWANATHAN, H. S., AJO-FRANKLIN, J., BIRKHOLZER, J. T., CAREY, J. W., GUGLIELMI, Y., HYMAN, J. D., KARRA, S., PYRAK-NOLTE, L. J., RAJARAM, H., SRINIVASAN, G., & TARTAKOVSKY, D. M.: From Fluid Flow to Coupled Processes in Fractured Rock: Recent Advances and New Frontiers. *In Reviews of Geophysics*, 60(1), (2022). <https://doi.org/10.1029/2021RG000744>

ZHANG, X., SPIERS, C. J., & PEACH, C. J.: Compaction creep of wet granular calcite by pressure solution at 28°C to 150°C. *Journal of Geophysical Research: Solid Earth*, 115, (2010). B09217. <https://10.1130/10.1029/2008JB005853>

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