size of each particle was assumed to coincide with the diameter of a sphere with same volume. For this purpose, the overall volume of each agglomerate  $V_{agg}$  was calculated as:

$$V_{agg} = \frac{\sum V_{sub-particles}}{n_{int}}$$
(2)

where  $V_{sub-particles}$  is the volume of the sub-particles in the agglomerate and  $n_{int}$  is the internal porosity of the agglomerate (here set equal to 0.36). Diametrical compression simulations revealed that the mean failure stress of an agglomerate is proportional to the average strength of the internal bonds,  $\sigma_n$ . In addition, the simulations pointed out that such approach enables the size dependence of the grain strength to be reproduced successfully during fragmentation. Specifically, the variation of the particle strength for a given reference grain size was captured by assigning randomly the bond strength in accordance with a probability distribution based on Equation (1).



Figure 1. (a) Close up view of an agglomerate before diametrical compression; (b) results of diametrical compression simulations for different particle sizes.

Once the particle strength variability in diametrical compression simulations was captured, 1D compression tests were simulated on agglomerate assemblies. Initially, assemblies consisting of rigid spherical particles were generated in a prismatic container based on a given porosity. Then, several computational timesteps were imposed to eliminate particle overlaps and reach a stable configuration. This task was carried out by allowing particles to rearrange with zero inter-particle friction. Then, each rigid particle was replaced with a crushable agglomerate composed of bonded spherical sub-particles. After the generation of agglomerates, the final contact parameters were assigned and additional computational steps were applied to reach a

stable configuration before loading. 1D compression was implemented by moving the top and bottom axial walls towards the specimen. The progression of bond breakage events and the accumulation of deformations were examined during the compression process. DEM simulations were carried out by using a linear parallel bond model with the method of deformability which relates macroscopic elastic parameters of the specimen such as the Young's modulus to microscopic parameters (see Itasca (2014)). Therefore, the model parameters were determined based on the elastic properties of the selected proppant. Although different proppant types (e.g., sand, resin coated sand and ceramic) are employed in hydraulic fracturing applications, this study focused on the mechanical behavior of sand proppants because of its common usage. A summary of the DEM model parameters is listed in Table 1.

### **1D COMPRESSION SIMULATION RESULTS**

Hereafter, two types of packing (i.e., multi-layer and mono-layer) usually observed in hydraulic fracturing operations were considered to identify the influence of packing conditions on their compression/fracture behavior. The initial packing configuration of each simulation is showed in Figure 2. In multi-layer packings, 5-7 times more layers were present along the vertical direction compared to mono-layer packings. Both simulations extended along the horizontal direction to replicate a small section of a long fracture filled with proppants.

Parameter	Value
General model properties	
Agglomerate size (D <sub>min</sub> - D <sub>max</sub> )	0.8 mm - 1.5 mm
Initial specimen porosity	0.49 (Multi-layer packing) 0.58 (Mono-layer packing)
Linear contact parameters	
Effective stiffness	70 GPa
Stiffness ratio (k <sub>n</sub> /k <sub>s</sub> )	1.0
Friction coefficient	0.5
Parallel bond parameters	
Installation gap	D <sub>min</sub> /34
Radius multiplier	1.0
Bond effective stiffness	70 GPa
Bond stiffness ratio	1.0
Cohesion	$\sigma_n * 10$
Weibull function parameters	
Reference particle size $(d_0)$	2.0 mm
Characteristic bond strength ( $\sigma_0$ )	50 MPa
Weibull modulus w	3.3

Table 1. Summary of the DEM model parameters





The deformation response obtained from 1D compression simulations is shown in Figure 3, where the evolution of the axial stress acting on the packing is plotted as a function of axial strains and displacements. Agglomerates in mono-layer packing had limited possibility to rearrange at the beginning of the compression stage, having that breakage events can lead to considerable stress fluctuations. By contrast, in multi-layer packings the stress increased more gradually during the initial stages of loading, until achieving the onset of substantial grain breakage, after which a limited variation in stress upon increasing compressive strains was found and larger stress fluctuations were observed. Also in the latter case, the stress fluctuations can be attributed to the small number of particles in the analyses. It is worth noting that the agglomerates in multi-layer packings, thus stressing the role of a range of grain-scale phenomena, as particle rearrangement and force redistribution in the definition of the performance of the different packing configurations.



Figure 3. Stress-strain and stress-displacement relationships resulting from 1D compression simulations.

The distribution of produced fragments as a result of agglomerate breakage is showed in Figure 4, which illustrates that breakage events tended to occur randomly throughout the specimen in both simulations. In the mono-layer packing, fragments appear at discrete locations, possibly because of early fractures taking place in particles in contact with the fracture walls, where the largest fraction of axial forces are sustained. By contrast, in the multi-layer packing agglomerate fractures occurred at the interface between specimen and loading walls, as well as within the specimen.



Figure 4. Distribution of fragments generated at the end of the simulated stage of compression in (a) multi-layer and (b) mono-layer packing. Broken agglomerates are highlighted and the rest of the specimen is shown with transparent shading.

Since the goal of proppant placement in hydraulic fracturing is to guarantee high hydraulic conductivity under sustained in situ compressive stresses, it is important to keep track of the fines that may be generated during the fracture closure stage, which may indeed have detrimental consequences for the overall success of the placement intervention. To examine the process of fines generation upon compression-induced crushing with the proposed DEM model, the evolution of the particle size distribution (PSD) has been tracked for the two different packing configurations considered in the previous section. Such analysis are summarized in Figure 5. The results indicate that in both cases the amount of fine particles gradually increased during the compression process. At any given strain level, the fines content resulted to be slightly higher in the multi-layer packing than in the mono-layer packing, which may be a consequence of the higher stresses to which proppant packings were subjected at comparable strain levels. However, if the same property is inspected at fixed stress level (e.g., a constant stress imparted by the surrounding rock formation) as well as for a fixed amount of fracture closure (i.e., by plotting the PSD as a function of the axial displacement), it is possible to notice that the change of the PSD in the case of a multi-layer packing was negligible small compared to that computed for the mono-layer system.

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Figure 5. Evolution of the particle size distribution (PSD) at given levels of (a) axial strains and (d) axial displacements (i.e., fixed amount of fracture closure).

### CONCLUSIONS

The deformation/crushing characteristics of proppants were investigated using 3D DEM simulations. The bond strength of numerical agglomerates was assigned via a Weibull statistics to capture the size-dependency of the particle strength that is often observed in diametrical compression tests. The stress-strain response and particle size evolution for simulations based on different packing configurations (i.e., multi-layer and mono-layer) have been examined. The results indicate that multi-layer packings may sustain higher compressive stresses compared to mono-layer packings, as well as that they can mitigate the production of fines generated by confined comminution at constant levels of applied stress and/or fracture closure. The simulations also revealed that increasing axial stresses may result in considerable grain breakage and alterations of the PSD of the proppant packing. Such micro-scale analyses provide insight on the evolution of fragmentation in granular media subjected to extreme stress conditions

and have the potential to assist the design/selection of granular proppants to be used for hydraulic fracture interventions under site-specific reservoir conditions.

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### Thermo-Hydro-Chemo-Mechanical Formulation for CH<sub>4</sub>-CO<sub>2</sub> Hydrate Conversion Based on Hydrate Formation and Dissociation in Hydrate-Bearing Sediments

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Abstract: Gas production from gas hydrate-bearing sediments has been attracting global interests because of its potential to meet growing energy demand. Methane (CH<sub>4</sub>) gas can be extracted from CH<sub>4</sub> hydrates by depressurization, thermal stimulation or chemical activation. However, it has never been produced on a commercial scale and the past field trials faced premature termination due to the technical difficulties such as excessive sand flow into the well, a phenomenon known as sand production. One exception is the trial at the Ignik Sikumi, Alaska in 2012, which was conducted by chemical activation followed by depressurization. During the trial, initial sand production ceased after two weeks while CH<sub>4</sub> gas production continued for five weeks. The mitigation of sand production is deemed attributed to mechanical or hydraulic effects through formation of CO<sub>2</sub>-rich gas hydrates. This incident has highlighted the favorable effect of CO<sub>2</sub> hydrate formation and needs to incorporate the chemo-processes into existing thermo-hydro-mechanical formulations. This paper analytical formulation the coupled presents an to capture thermo-hydro-chemo-mechanical behavior of gas hydrate-bearing sediments during gas production via CO<sub>2</sub> injection. The key features of the formulation include hydrate formation and dissociation, gas dissolution and multiphase flow for both CH<sub>4</sub> and CO<sub>2</sub>, facilitating CH<sub>4</sub>-CO<sub>2</sub> hydrate conversion.

#### BACKGROUND

CH<sub>4</sub> hydrate has been attracting growing international interest because of its potential as an abundant and widespread source of natural gas that could provide nations with long term energy security. Conservative estimates suggest that more than 10 trillion m<sup>3</sup> of CH<sub>4</sub> gas resides in oceanic gas hydrate deposits throughout the globe, exceeding the known volume of technically recoverable remaining conventional natural gas (e.g. Burwicz et al., 2011; Milkov, 2004). An economic means of extracting gas from gas hydrate-bearing sediments could therefore meet many decades worth of global energy demand. Three methods have been proposed as being feasible for hydrate dissociation (i.e. phase change of CH<sub>4</sub> from hydrate into gas) at in-situ: [1] depressurization – the use of depressurized wells to reduce the pressure in the soil around the wells; [2] thermal stimulation – the use of thermal injection well to increase the temperature in the surrounding soil; and [3] chemical activation – the use of CO<sub>2</sub> injection to release the CH<sub>4</sub> gas from the hydrate and convert it into more stable CO<sub>2</sub> hydrate.

To date, only a few short-term field trials of gas production from hydrate-bearing sediments have been reported, most notably the trials conducted at the Mallik gas hydrate site, Canada, in 2007 (Dallimore et al., 2008), at the Ignik Sikumi well, Alaska, in 2012 (Schoderbek et al., 2013) and at the Eastern Nankai Trough, Japan in 2013 (Yamamoto, 2014). During these trials, gas extraction via depressurization encountered sand production problems, leading to a premature termination of the trials in 2007 and 2013. In contrast, during the trial in 2012, gas production was operated by depressurization plus chemical activation by  $CO_2/N_2$  injection and it is found that the initially occurred sand production ceased after two weeks while gas production continued for five weeks. Although the mechanism is yet to be fully understood, it is proposed that the stabilization of sand production during the 2012 trial was attributed to  $CO_2$  hydrate formation.

For sustainable gas exploitation from hydrate-bearing sediments in the future, therefore, an implementation of realistic mechanical behavior of hydrate-bearing sediments into thermo-hydro models was and still remains the next logical progression. As of today, a limited number of coupled thermo-hydro-mechanical formulations for behavior of hydrate-bearing sediments are available (e.g. Kim et al., 2011; Kimoto et al., 2010; Klar et al., 2013). However, these formulations only deal with the dissociation process induced by depressurization or thermal stimulation and no analytical work exists to capture the chemical activation induced thermo-hydro mechanical process during hydrate dissociation. This paper presents a first step towards completing an analytical framework to capture the coupled behavior of gas hydrate-bearing sediments during gas production via chemical activation.

# MASS BALANCE EQUATIONS INCLUDING METHANE AND CARBON DIOXIDE

Methane exists as  $CH_4$  hydrate, aqueous  $CH_4$  and gaseous  $CH_4$ . Likewise, carbon dioxide can exist as  $CO_2$  hydrate, aqueous  $CO_2$ , gaseous  $CO_2$  and liquid  $CO_2$ . For simplicity, this study assumes that the gaseous phase and liquid phase of  $CO_2$  are indistinguishable. This implies that liquid  $CO_2$  behaves identically to that of gaseous

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 $CO_2$ . In this study,  $CH_4$  hydrate is denoted as "*mh*", aqueous methane as "*mw*" and gaseous methane as "mg", CO<sub>2</sub> hydrate as "ch", aqueous CO<sub>2</sub> as "cw" and gaseous/liquid CO<sub>2</sub> as "*cg*".

There are two phenomena changing the phase of methane or carbon dioxide: hydrate formation/dissociation and gas dissolution. Methane (or carbon dioxide) hydrate consists of one molecule of  $CH_4$  (or  $CO_2$ ) and  $N_{mh}$  (or  $N_{ch}$ ) molecules of pure water. For simplicity, this study assumes that the hydrate forms only from the gaseous phase and thus dissociation releases only gaseous methane (or carbon dioxide). This implies hydrate formation/dissociation does not affect  $m_{mw}$  (or  $m_{cw}$ ) where m is the mass per control volume. On the other hand, gas dissolution increases  $m_{mw}$  (or  $m_{cw}$ ) and decreases  $m_{mg}$  (or  $m_{cg}$ ). Introducing the rate of gas dissolution  $R_{mw}$  (or  $R_{cw}$ ) and that of hydrate formation/dissociation  $R_{mh}$  (or  $R_{ch}$ ), formation positive and dissociation negative, the mass balance equations of pure water, aqueous CH<sub>4</sub> and aqueous CO<sub>2</sub> can be expressed as:

$$dm_{w(pure)} = -\nabla \cdot \left(\rho_{w(pure)} \mathbf{q}_{w(pure)}\right) dt - N_{mh} M_{w(pure)} R_{mh} dt - N_{ch} M_{w(pure)} R_{ch} dt \tag{1}$$

$$dm_{mm} = -\nabla \cdot \left(\rho_{mm} \mathbf{q}_{mm}\right) dt + m_m R_{mm} dt \tag{2}$$

$$dm_{mw} = -\nabla \cdot (\rho_{mw} \mathbf{q}_{mw}) dt + m_w R_{mw} dt$$
<sup>(2)</sup>

$$dm_{cw} = -\nabla \cdot (\rho_{cw} \mathbf{q}_{cw}) dt + m_w R_{cw} dt \tag{3}$$

where the subscript w(pure) represents pure water,  $\rho$  is the density, **q** is the discharge, M is the molecular mass and t is the time. The rate R is approximated by a first-order kinetics and described in the next section. Similarly, the mass balance equations of gaseous CH<sub>4</sub> and CO<sub>2</sub> are:

$$dm_{mg} = -\nabla \cdot \left(\rho_{mg} \mathbf{q}_{mg}\right) dt - M_{mg} R_{mh} dt - m_{w} R_{mw} dt \tag{4}$$

$$dm_{cg} = -\nabla \cdot (\rho_{cg} \mathbf{q}_{cg}) dt - M_{cg} R_{ch} dt - m_w R_{cw} dt$$
<sup>(5)</sup>

The mass balance equations of the two pure hydrates are:

$$dm_{mh} = N_{mh}M_{w(pure)}R_{mh}dt + M_{mg}R_{mh}dt$$
(6)

$$dm_{ch} = M_{ch}M_{w(pure)}R_{ch}dt + M_{cg}R_{ch}dt$$
<sup>(7)</sup>

Formation of mixed CH<sub>4</sub>-CO<sub>2</sub> hydrates is not explicitly considered in this study.

Both the aqueous CH<sub>4</sub> and CO<sub>2</sub> and gaseous CH<sub>4</sub> and CO<sub>2</sub> are treated as fully miscible, resulting in an aqueous CH<sub>4</sub>-CO<sub>2</sub> mixture and a gaseous CH<sub>4</sub>-CO<sub>2</sub> mixture. In other words, these mixtures can be represented as a single material:

$$dm_w = dm_{w(pure)} + dm_{mw} + dm_{cw}$$
(8)

$$dm_g = dm_{mg} + dm_{cg} \tag{9}$$

where the subscripts w and g represent the aqueous  $CH_4$ - $CO_2$  mixture and the gaseous CH<sub>4</sub>-CO<sub>2</sub> mixture, respectively. This study assumes that Darcy's law is valid for the mixtures controlled by the mixture pressure. Since the mixture behaves together, the discharge for each component holds the same quantity as that of the mixture:

$$\mathbf{q}_{w} = -\frac{\mathbf{K}_{h}}{\mu_{w}} k_{w}^{r} (\nabla P_{w} - \rho_{w} \mathbf{g}) = \mathbf{q}_{w(pure)} = \mathbf{q}_{mw} = \mathbf{q}_{cw}$$
(10)

$$\mathbf{q}_{g} = -\frac{\mathbf{K}_{h}}{\mu_{g}} k_{g}^{r} (\nabla P_{g} - \rho_{g} \mathbf{g}) = \mathbf{q}_{mg} = \mathbf{q}_{cg}$$
(11)

where  $\mu$  is the viscosity,  $k^r$  is the relative permeability factor, P is the pressure, g is the gravitation vector and  $\mathbf{K}_{h}$  is the intrinsic permeability tensor of the hydrate-sediments. The density of each component in the mixture is defined as the mass concentration of its component (i.e. mass of a constituent divided by the volume of the mixture):

$$\rho_{w} = \rho_{w(pure)} + \rho_{mw} + \rho_{cw} = \frac{1}{nS_{w}} \left( m_{w(pure)} + m_{mw} + m_{cw} \right)$$
(12)

$$\rho_{g} = \rho_{mg} + \rho_{cg} = \frac{1}{nS_{g}} \left( m_{mg} + m_{cg} \right)$$
(13)

## KINETIC MODELS FOR GAS DISSOLUTION, HYDRATE FORMATION AND HYDRATE DISSOCIATION

Dissolution for gaseous phase substances into their aqueous phase is assumed to be driven by the difference between the maximum mass concentration of the aqueous solute and the current mass concentration of aqueous solute. Thus, the rates of dissolution for  $CH_4$  and  $CO_2$  can be obtained by:

$$R_{mw} = D_{mw} \left\langle c_{mw(max)} - \frac{m_{mw}}{m_{w}} \right\rangle$$
(14)

$$R_{cw} = D_{cw} \left\langle c_{cw(\max)} - \frac{m_{cw}}{m_w} \right\rangle$$
(15)

where  $c_{mw(max)}$  and  $c_{cw(max)}$  are the maximum mass concentrations above which no dissolution occurs for gaseous CH<sub>4</sub> and CO<sub>2</sub> respectively, *D* is the rate of dissolution coefficient (i.e. the phase transition coefficient multiplied by the volumetric specific liquid-gas surface area) and  $\langle \cdot \rangle$  is the Macaulay bracket. The above rates are expressed in a control volume.

Formation and dissociation of gas hydrate is assumed to be governed by first-order kinetics, controlled by partial pressures of gaseous  $CH_4$  and  $CO_2$ , rather than the total gas pressure. The partial pressure (molar fraction) of each gas is given by:

$$P_{mg} = \frac{m_{mg} / M_{mg}}{m_{mg} / M_{mg} + m_{cg} / M_{cg}} P_g = \frac{m_{mg} M_{cg}}{m_{mg} M_{cg} + m_{cg} M_{mg}} P_g$$
(16)

$$P_{cg} = \frac{m_{cg} M_{mg}}{m_{mg} M_{cg} + m_{cg} M_{mg}} P_g$$
(17)

Thus, the rate of hydrate formation and dissociation in moles per control volume (formation positive) can be expressed by:

$$R_{mh} = nS_g K_{mh}^f A_{mh}^s \left\langle P_{mg} - P_{mh}^{eq} \right\rangle - nS_{mh} K_{mh}^d A_{mh}^s \left\langle P_{mh}^{eq} - P_{mg} \right\rangle$$
(18)

$$R_{ch} = nS_g K_{ch}^f A_{ch}^s \left\langle P_{cg} - P_{ch}^{eq} \right\rangle - nS_{ch} K_{ch}^d A_{ch}^s \left\langle P_{ch}^{eq} - P_{cg} \right\rangle$$
(19)

where S is the saturation,  $K^{j}$  is the hydrate formation constant,  $A^{s}$  is the hydrate surface area for unit volume of the hydrate,  $P^{eq}$  is the phase-equilibrium pressure of hydrate dependent on temperature and  $K^{d}$  is the hydrate dissociation constant.