Quantifying the desaturation effect of biogenic gas formation in sandy soil

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ABSTRACT: Biogenic gas formation can be applied as a ground improvement method for applications such as liquefaction mitigation, as inducing a gas phase in a saturated soil reduces the bulk stiffness during undrained loading. Denitrification is one of the processes to produce biogenic gas in the soil through the dissimilatory nitrate reduction to (di)nitrogen gas. In this study a simplified model was used to predict the desaturation induced by denitrifying bacteria, which produce nitrogen gas when supplied with a substrate solution containing calcium acetate and calcium nitrate as growth substrates. The model shows that the gas volume is strongly dependent on pressure conditions, but for most applications a single injection of substrate solution with nitrate concentration of only 1.2 g per litre is sufficient, considering that only a 5% reduction of water saturation ($S_w$) is sufficient to mitigate liquefaction. The gas can be distributed as single bubbles or be mobile and rapidly accumulate. Soil properties and environmental conditions affect the formation and stability of gas phase in the soil. Results of triaxial tests confirmed that pressure conditions, the amount of produced gas in relation to the gas storage capacity of the sand directly affect formation and stability of the gas phase.

1 INTRODUCTION

Introducing gas into soil to reduce the degree of saturation is shown to be useful to increase the soil resistance to dynamic loading and helps to mitigate liquefaction. There are several methods to generate the partially saturated conditions such as gas injection (Okamura et al. 2011), water electrolysis (Yegian et al. 2007), and production of gas in situ through a chemical process (Yegian et al. 2012). Using biogenic gas through denitrification is another approach that also is reported to be feasible (Rebata-Landa et al. 2011, He et al. 2014, van Paassen et al. 2010a, Kavazanjian et al. 2015, O’Donnell, 2016).

Denitrification is the dissimilatory nitrate reduction pathway of nitrate NO3- in the nitrogen cycle, in which NO3- is reduced to N2 gas through the intermediates of NO2-, NO and N2O (Knowles 1982). Besides N2 gas, the reaction produces carbonate, which increases the alkalinity of the soil. In presence of dissolved calcium, CaCO3 will precipitate, which neutralizes the increase in alkalinity. This coupled process helps to maintain pH of the environment around neutral (pH7) and limits the accumulation of unwanted denitrification intermediates, making N2 gas and CaCO3 the end products of the process (Pham et al. 2016). This bio-based approach has potential for a wide range of soil improvement applications (Khodadadi et al. 2017). Microbially induced carbonate precipitation, MICP, in soil strengthening has been well studied and successfully demonstrated at large scale (DeJong et al. 2009, Van Paassen et al. 2010b, van Paassen 2011, Burbank et al. 2011). Microbially induced desaturation and precipitation, MIDP, is the output of the coupled denitrification – precipitation process and has been suggested as a two-stage method, capable for strengthening or liquefaction mitigation (O’Donnell et al. 2016). For liquefaction mitigation, soil strengthening by CaCO3 precipitation (van der Star et al. 2009) is an added advantage of the MIDP method in comparison with the others.

Applications using the N2 gas requires the ability to evaluate and control the gas distribution, stability and durability. Natural gas formation in practice has shown a risk of blow-out of gas clusters in sea bed and may threaten foundation stability of offshore installations (Hovland et al. 1988). An unstable gas phase can potentially trigger liquefaction rather than mitigating liquefaction (Grozic et al. 1998). Therefore predicting the amount of produced gas and evaluate its stability are important in order to apply the method into practice and design of treatment procedures.

For this purpose, this paper proposes a calculation method to estimate the produced gas volume and the resulting degree of saturation for the denitrification reaction in the MIDP process using denitrifi-
fication. The method is based on a thermodynamic approach, which allows to determine the stoichiometry of the metabolic reaction and the produced yield of N\textsubscript{2} and total inorganic carbon. Then the amount of N\textsubscript{2} and inorganic carbon gas speciation in the aqueous phase and equilibria between gas and aqueous phase are calculated following Henry’s law. The volume of gas is calculated using the ideal gas law. Finally, mass and volume balance over the pore volume are assumed to estimate the gas and water saturation in the soil. To validate the calculation method and study the gas formation, experiments were performed on a fine sand at different pressure conditions using a triaxial test set-up.

2 GAS PRODUCTION ESTIMATION

2.1 Assumptions and parameters of the gas estimation calculation

Assumptions of the calculation

A simplified calculation method is proposed to estimate the amount of gas production by MIDP and its effect on the degree of saturation, using the following assumptions:

1. NO\textsubscript{3} is reduced completely to N\textsubscript{2}, accumulation of the intermediates of denitrification is not considered.
2. The pore gas pressure equals the pore water pressure in the soil, thus the effect of surface tensions and capillarity are neglected.
3. The soil is initially fully saturated and the total volume is assumed to be constant, so there is no deformation of the samples during the experiments.
4. pH is constant around neutral.

Reaction stoichiometry

The stoichiometry of the denitrification reaction using acetate C\textsubscript{2}H\textsubscript{3}O\textsubscript{2} as the energy and carbon source and nitrate as oxidizing agent and nitrogen source is calculated using the thermodynamic approach suggested by Heijnen et al. (2010), based on two extreme scenarios, which are no growth or maximum growth. For maximum growth conditions the stoichiometry of denitrification is (Pham et al. 2016):

\[
\text{1.21 C}_2\text{H}_3\text{O}_2^- + 0.97 \text{NO}_3^- + 0.76 \text{H}^+ \rightarrow \\
\text{1CH}_3\text{O}_2\text{O}_3 + 1.41\text{HCO}_3^- + 0.39\text{N}_2 + 0.59\text{H}_2\text{O} 
\]

and for conditions of no biomass growth, but only maintenance:

\[
\text{C}_2\text{H}_3\text{O}_2^- + 1.6 \text{NO}_3^- + 0.6 \text{H}^+ \rightarrow \\
0.8\text{N}_2 + 2\text{HCO}_3^- + 0.8 \text{H}_2\text{O} 
\]

At any metabolic state of the denitrifying organisms, the reaction stoichiometry is between these two boundaries. Accordingly, the expected range of N\textsubscript{2}/NO\textsubscript{3} ratio is between 0.40 and 0.50, and the ratio of HCO\textsubscript{3}/NO\textsubscript{3} is between 1.45 and 1.25, corresponding with the boundary of maximum growth and no growth respectively. With these ratios, ranges of produced N\textsubscript{2} and HCO\textsubscript{3} can be calculated when the consumed concentration of NO\textsubscript{3} is known:

\[
c_{\text{N}_2}^{\text{tot}} = \frac{\text{N}_2}{\text{NO}_3^-} \cdot c_{\text{NO}_3^-} \quad (1)
\]

\[
c_{\text{HCO}_3^-}^{\text{tot}} = \frac{\text{HCO}_3^-}{\text{NO}_3^-} \cdot c_{\text{NO}_3^-} \quad (2)
\]

where \(c_{\text{N}_2}^{\text{tot}}\) is the total produced mol-N\textsubscript{2} per L of liquid; \(c_{\text{HCO}_3^-}^{\text{tot}}\) is the total produced mol-HCO\textsubscript{3} per L of liquid; \(c_{\text{NO}_3^-}^{\text{consumed}}\) is the consumed mol-NO\textsubscript{3} per L of liquid.

N\textsubscript{2} and HCO\textsubscript{3} in the gas-liquid phase equilibrium

The produced N\textsubscript{2} is distributed between the gaseous and dissolved form following Henry’s law:

\[
e_{\text{N}_2}^{\text{ad}} = \frac{P_{\text{N}_2}}{K_{\text{H,N}_2}} \quad (3)
\]

\[
n_{\text{N}_2}^{\text{aq}} = (e_{\text{N}_2}^{\text{tot}} - e_{\text{N}_2}^{\text{ad}}) \times V_L \quad (4)
\]

where \(e_{\text{N}_2}^{\text{ad}}\) is the dissolved concentration of N\textsubscript{2} in mol-N\textsubscript{2} per L liquid; \(P_{\text{N}_2}\) is the partial pressure of N\textsubscript{2} gas; \(K_{\text{H,N}_2}\) is Henry coefficient of N\textsubscript{2} gas which is 1542.6 atm L mol\textsuperscript{-1} at 298K; \(n_{\text{N}_2}^{\text{aq}}\) is the amount of N\textsubscript{2} gas in moles; \(V_L\) is the liquid volume, which is assumed to be equal to the pore volume of the soil, as the result of assumption 3.

The produced HCO\textsubscript{3} is in equilibrium with carbonic acid (H\textsubscript{2}CO\textsubscript{3}*) according to:

\[
\frac{c_{\text{H}^+} \cdot c_{\text{HCO}_3^-}}{c_{\text{H}_2\text{CO}_3^*}} = 10^{-6.35} \quad (5)
\]

And with carbonate (CO\textsubscript{3}^2-) according to:

\[
\frac{c_{\text{H}^+} \cdot c_{\text{CO}_3^{-2}}}{c_{\text{HCO}_3^-}} = 10^{-10.33} \quad (6)
\]

Equilibrium constant at 298K are from Mines (2014). The carbonic acid (H\textsubscript{2}CO\textsubscript{3}*) is assumed to represent the dissolved CO\textsubscript{2}, which is in equilibrium with the gas phase following Henry’s law:

\[
e_{\text{CO}_2}^{\text{aq}} = \frac{P_{\text{CO}_2}}{K_{\text{H,CO}_2}} \quad (7)
\]

In which, \(K_{\text{H,CO}_2}\) is Henry’s coefficient for CO\textsubscript{2} which is 29.51 atm L mol\textsuperscript{-1} at 298K.
strates are provided as calcium salts the produced inorganic carbon will precipitate with the dissolved calcium ions as CaCO$_3$ as soon as the ionic activity product exceeds the solubility product. It is assumed that the solution is in equilibrium with the solid CaCO$_3$:

$$c_{Ca^{2+}} \times c_{CO_3^{2-}} = 10^{-8.47}.$$  

(8)

The total inorganic carbon is equal to the sum of all these chemical species, which follows from Eq.2:

$$c_{HCO_3^{--}} \cdot V_L = n_{CO_2^g} + n_{CaCO_3} + \left( c_{H_2CO_3} + c_{HCO_3^-} + c_{CO_3^{2-}} \right) \times V_L.$$  

(9)

where $n_{CO_2^g}$ = amount of CO$_2$ gas in moles; $n_{CaCO_3}$ = amount of precipitated CaCO$_3$ in moles, which is the difference between the total Ca$^{2+}$ and the amount that stays in equilibrium with CO$_3^{2-}$:

$$n_{CaCO_3} = \left( c_{Ca^{2+}} - c_{Ca^{2+}}^{\text{sat}} \right) \times V_L.$$  

(10)

Accordingly, the amount of CO$_2$ gas can be calculated using equation (9). The amount of CO$_2$ gas depends on the pH of the environment. The observed pH range during MIDP experiments is between 6.3 and 7.2 (van Paassen et al. 2010, O’Donnell 2016, Pham et al. 2016). To estimate the maximum possible CO$_2$ gas production, the lower boundary pH-value of 6.3 was selected for the calculation.

Calculating the total gas volume and the gas saturation in the soil

From the calculation of $n_{N_2^g}$ and $n_{CO_2^g}$, the total volume of gas, $V_g$, is calculated as:

$$V_g = \frac{\left( n_{N_2^g} + n_{CO_2^g} \right) \times R \times T}{p_g}.$$  

(11)

Where $R$ is the universal gas constant (8.314 kJ mol$^{-1}$ K$^{-1}$); $T$ is the temperature (298K); $p_g$ is the gas pressure. For a mixture of CO$_2$ and N$_2$ gas, the gas pressure is the sum of the partial pressures:

$$p_g = p_{N_2} + p_{CO_2}.$$  

(12)

Assumption (3) results in the following relation:

$$p_g = p_w.$$  

(13)

where $p_w$ is the pore water pressure of the soil, which is assumed to be hydrostatically related to the groundwater level.

The gas saturation, $S_g$, is calculated as:

$$S_g = \frac{V_g}{V_{pores}} \times 100\%.$$  

(14)

In this calculation, the unknown are $n_{N_2^g}$, $n_{CO_2^g}$, $p_{N_2}$ and $p_{CO_2}$ and can be found corresponding with $p_w$, $c_{NO_3^-}$ assumed and pH by iterative calculation, ensuring that the equations (10) and (13) are satisfied.

2.2 Calculated gas saturation

The calculation is applied for a pressure range of 1-3.5 atm, corresponding to depths ranging from 0 to 25 meter below with the groundwater level. Three different NO$_3^-$ concentrations were used: 20 mM, 50 mM and 100 mM. Expected ranges of the gas saturation between the two stoichiometry extremes are presented in Figure 1.

![Figure 1](image-url)  

Figure 1. Expected gas saturation by MIDP in sandy soil.

The results indicate that the induced gas saturation by MIDP is strongly dependent on the pressure conditions and the amount of converted NO$_3^-$, while it is less sensitive to the stoichiometry of the denitrification reaction. The difference when considering CO$_2$ in the calculation proved to be insignificant, therefore it was assumed that formation of a CO$_2$ gas component can be neglected in a simplified gas calculation of MIDP process.

This calculation suggests that using 20 mM NO$_3^-$ or 1.2 g-N$_2$/L is sufficient for the application of liquefaction mitigation, considering that about 5% gas saturation can already significantly reduce the liquefaction risk (He et al. 2013).

3 TRIAXIAL TEST EXPERIMENTS

To validate the model above, denitrification experiments were performed in a modified triaxial test setup.

3.1 Experiment set-up and variables

Gas production by MIDP process in sandy soil was measured by using a modified triaxial test set-up, as presented in Figure 2, similarly to the description in
standard ISO/TS 17892-9:2004 (CEN, 2004). Experiments were performed on a fine ‘Baskarp’ sand (Sibelco), which had $d_{50}$ is 0.123mm. Details of the experiment variables are presented in Table 1 together with the results of the gas saturation at the end of experiments.

<table>
<thead>
<tr>
<th>Pore – Cell pressure (kPa)</th>
<th>Bulk density ($g/cm^3$)</th>
<th>Porosity [%]</th>
<th>Relative density [%]</th>
<th>Gas saturation After reaction [%]</th>
<th>Gas saturation After flushing [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-100</td>
<td>1.50</td>
<td>43.3</td>
<td>39.5</td>
<td>24.2</td>
<td>17.8</td>
</tr>
<tr>
<td>50-150</td>
<td>1.51</td>
<td>42.9</td>
<td>43.1</td>
<td>21.8</td>
<td>7.9</td>
</tr>
<tr>
<td>100-200</td>
<td>1.54</td>
<td>42.8</td>
<td>43.4</td>
<td>22.3</td>
<td>2.4</td>
</tr>
<tr>
<td>250-300</td>
<td>1.52</td>
<td>42.6</td>
<td>45.6</td>
<td>15.6</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Table 1. Sand properties and results of the gas saturation with a single treatment of 50 mM nitrate

Figure 2. Modified triaxial test set-up

Samples were prepared using a split mould mounted with a rubber membrane inside (inner diameter 65mm, height 130mm). 250 mL liquid suspension was prepared containing 30mM Ca(C$_2$H$_3$O$_2$) – 25mM Ca(NO$_3$)$_2$, 40 mL/L inoculum containing denitrifying bacteria suspension, and other nutrients and trace elements as described in the experiments of (van Paassen et al. 2010). The suspension and the sand were poured into the mould in turns keeping the sand always submerged. After filling the mould, the sample was closed with porous stone and top cap. The triaxial cell was installed and filled with water to apply the cell pressure on the sample. The sample was then saturated following the instruction in ISO/TS 17892-9:2004, and the back and cell pressure was increased stepwise to the tested values. Duration of the experiments was about 10 days, in which the back valve was opened so expelled water due to the gas production inside the samples was collected in the back pressure controller. By continuously measuring the volume of the expelled liquid, the gas production rate was directly evaluated, and gas and water saturation inside the samples were calculated accordingly. After the reaction phase, the samples were flushed under a constant head of 1.5m water pressure by the third controller connected to the bottom of the samples. Change of the water and gas saturation after washing was measured to estimate the stability of the gas phase. Another experiment was performed to evaluate the gas stability after multiple treatment cycles. This experiment was executed at 100 kPa back pressure – 200 cell pressure, in which a sand column was flushed 15 times with a substrate solution containing 12mM Ca(C$_2$H$_3$O$_2$) and 10mM Ca(NO$_3$)$_2$, before being flushed with water.

3.2 Results and discussion

A common profile of water desaturation was observed for all tests, as shown in Figure 3: Gas production rate increased gradually in time until a threshold was reached above which the produced gas vented out of the sample and no longer desaturate the soil. This threshold corresponds with a gas saturation of 22%-25%. The test at the highest pressure of 250 kPa back pressure and 300 kPa cell pressure, the gas production profile and consequently the water desaturation profile had a smooth transition toward the end of the experiment and did not reach this gas percolation threshold. The gas production rate also showed to be dependent on the pressure conditions of the samples.

Figure 3. Water saturation of the samples due to the gas production

Stability of the gas phase was evaluated based on the change of the gas saturation during flushing at the end of the experiments. Results are presented in Table 1. The gas was the most stable for the case of 250 kPa back pressure and 300 kPa cell pressure in which the gas production did not reach the threshold. For the other cases, flushing at a constant head dif-
ference of 1.5m water significantly reduced the gas saturation as the induced gas phase got displaced by water. In the test at 100 kPa back pressure and 200 kPa cell pressure almost all the induced gas was flushed away.

In the long-term experiment in which the sand was flushed 15 times with 12mM Ca(C\textsubscript{2}H\textsubscript{3}O\textsubscript{2}) \textsubscript{2} \textendunderline{–} 10mM Ca(NO\textsubscript{3})\textsubscript{2} at 100 kPa back pressure – 200 cell pressure, the maximum gas saturation was also about 22%. Flushing under constant head of 1.5m water pressure after each treatment replaced about half of the induced gas phase resulting and about 10% gas saturation remained after flushing throughout the experiment (Pham et al. 2017).

The experimental results show that the volume of the gas and the related gas saturation are defined by the amount of converted substrate, the pressure conditions and the percolation threshold of the soil. The converted substrate amounts, the hydraulic pressure conditions and the specific growth rate (at maximum growth rate, no growth, or in between) of the denitrifying bacteria are the variables that determine the total gas volume to be produced, but the soil matrix and confining pressure conditions determine the amount of gas which remains in the soil and its stability. The existence of a gas percolation threshold is well established in scientific literature. The solid matrix may act as a nucleation site for gas bubble formation as well as entrapment for gas bubble agglomeration and transportation (Rebata-Landa et al. 2011, Brooks et al. 1964), which will affect the amount, size, shape and connectivity of the gas bubbles at micro scale (Gauglitz et al. 1989, Lee et al. 2004, Mosdorf et al. 2013). Once the gas forms a network of connected air pockets it can rapidly accumulate forming air filled pockets in the soil and find or create pathways venting upwards (Istok et al. 2007, Inès M. Soares et al. 1988). At this stage, the gas percolation threshold is reached and any additional produced gas will not remain in the soil. The gas dissolution rate is also determined by the confinement effect as it can influence the mass transfer inside the pores (Li et al. 1995). When the gas production is below the percolation threshold, the induced gas phase shows a high stability as seen in the result of the 250 kPa back pressure – 300 kPa cell pressure. This suggests that the percolation network was not completely developed. As a result, the major part of the gas remained as discrete bubbles in the pores during flushing.

4 COMPARING THE CALCULATED AND MEASURED GAS SATURATION

Figure 4 shows the combined results from the experiments and the calculation. The measured gas production falls within the calculated range when the produced amount of gas did not exceed the gas percolation threshold, i.e. in the case of 250 kPa back pressure and 300 kPa cell pressure. For the other cases, in which the gas production exceeded the percolation threshold and vented out, the total produced gas volume was not captured and therefore could not be used to validate the calculation.

Although the experiments did not meet the target of validating the calculation as these calculations did not take gas percolation into account, the overall results show that it is possible to predict the amount of produced gas as a function of substrate concentrations and pressure conditions. In order to limit formation of excess gas, obtain a stable gas phase and limit blow-out risk it is suggested to use the gas percolation threshold as an upper limit for the targeted level of gas saturation. While the percolation threshold is a soil characteristic, to obtain a target of gas saturation that does not exceed the threshold, the calculation method proposed in this chapter can be used as an engineering tool to determine the required substrate concentrations as a function of the environmental conditions of the treatment. Further experiments using different grain sizes and packing density need to be done to validate the calculation and study the influences of soil matrix to the gas stability and distribution. The model furthermore can be extended to predict pH and also include other acid-based equilibria needed for that.

![Figure 4. Comparing the calculated (grey) and measured gas (blue diamonds) saturation when 50 mM NO\textsubscript{3}\textsuperscript{-} was used](image-url)

5 CONCLUSIONS

Biogenic gas by denitrification in the MIDP process has the potential to mitigate soil liquefaction. The calculation method presented in this paper allows quantifying the produced gas volume and its desaturation effect in the soil. It shows that CO\textsubscript{2} gas can be neglected in a simplified gas calculation of MIDP. Experimental results indicate that considering the gas production in correspondence with the percolation threshold of the soil helps to evaluate the stability of the induced gas phase and limit the blow-out risk. Soil matrix and confinement conditions play an
important role in the gas production process and determine the gas percolation threshold.

6 ACKNOWLEDGEMENTS

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7 REFERENCES