

## The mitigation of deep depth wellbore leakage using microbially induced carbonate precipitation (MICP)

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### Summary

Leaks in the annular cement used to seal oil and gas wells are commonly fixed by, 'squeezing' a sealing material, commonly cement, in the annulus and surrounding rock. The effectiveness of this technique in certain environments, such as those in small aperture leakage pathways, has been questioned [3]. Bacterially induced mineral precipitates (e.g., calcium carbonate [CaCO<sub>3</sub>]) have been shown to be effective at sealing small aperture leaks and porous rocks at shallow depths (< 1km) [7]. We have extended this work in this study by examining bacteria capable of surviving at deep depth (> 1km), oxygen limited environments where temperature and pressure are higher. In particular, we designed and monitored a model biomineralization system with *Geobacillus thermodentrifican* for calcium carbonate production according to analog wellbore conditions. Few studies have investigated thermophilic bacteria for MICP and this is the first to examine a model system and bacterium for wellbore repair at deep depth-like conditions. Also, we modeled the system to understand and optimize the biomineralization medium for better cell growth, increased yield of calcium carbonate and reduced mineralization time. In this work, we showed that particular species (i.e., Ca<sup>2+</sup>(aq), PO<sub>4</sub><sup>3-</sup>(aq)) can be modeled to represent a biomineralization system in wellbore repair. Also, that *G. thermodentrificans* produced carbonates at analog deep depth wellbore conditions (i.e, high pressures, temperatures and gaseous conditions). These results can be helpful in further studies extending a system from bench to field scale conditions. Also, it provides proof of concept of an alternative repair technology to traditional repair techniques.

### Theory / Method / Workflow

Globally, a variable percentage of oil and gas wells develop leakage [1], of which methane is the predominant fluid. Leakage contributes to GHG emissions [2], may impair potable groundwater quality [1], and is costly to repair [3, 4]. Leakage pathways develop in the annular cement used to seal the space between steel casing(s) and the borehole face in response to poor cementing during well completion, and/or degradation and de-bonding of the cement over time [3, 5].

A promising repair technology is microbially induced calcite precipitation (MICP) in which the metabolic activity of bacteria is used to precipitate carbonates [6]. There are a variety of pathways by which this is achieved including ureolysis, iron reduction, sulfate reduction, fatty acid metabolism, carbohydrate catabolism (e.g. glucose, lactose, acetate), photosynthesis, methane oxidation and denitrification.

In general, as wellbore depths increase the temperature and pressure rises and the environment becomes more anaerobic. There is an opportunity to study the broader field applications of MICP as a wellbore remediation technology at these, 'extreme' [7] conditions.

With specificity to extremophilic bacteria, a promising set of species belonging to the genus *Geobacillus* has been identified by our group. They can act as denitrifiers and offer growth at higher temperatures. They were identified via a systemic analysis of growth conditions in both minimal and complex mediums to differentiate denitrifiers among starting species of the genera *Bacillus*, *Gracilibacillus*, *Geobacillus*, *Anoxybacillus* and *Pseudomonas*.

This report will describe efforts to better understand the effect of extremophilic denitrifiers on the mineralization of carbonates in solution, over time. Specifically, we monitored the changing chemistry of a biomineralization (i.e., 'cementation') solution following inoculation with a model bacterium, *Geobacillus thermodenitrificans*. Various aqueous, (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , etc.) and solid ( $\text{CaCO}_3$ , etc.) species were tracked. A figure modeling relationships of select species and/or other parameters is provided (Figure 1). These were used to build a model of the mineralization system with PHREEQC. In addition, insight was gained on high (i.e., > 10% change) and low (< 10% change) cycling species to aid bacterial growth optimization and understand mineral formation. In particular, the analysis of precipitates from solution provided an opportunity to observe the types of carbonates (and other minerals) produced ( $\text{CaCO}_3$ , Ca-phosphates, halite, etc).

Overall, this work provides a bench-scale investigation towards running, modeling and understanding the opportunities to optimize the conditions of denitrification for MICP in material repair; the specific application for leaky wellbore in deep depth environments.

## Results, Observations, Conclusions

### Biomineralization Experiments

Experiments were performed at 60°C in 150mL Wheaton bottles using 100mM calcium and 110mM  $\text{NaNO}_3$  in a modified, anaerobic Lysogeny Broth (LB) medium (10 g/L tryptone, 5 g/L yeast extract, 10 g/L  $\text{NaCl}$ , 0.0015M Nitritotriacetic acid, 0.00059M  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.00091M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.00004M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , pH 7.4). Of note, the starting concentration of calcium differed in solution due to the precipitation of calcium, potentially as calcium phosphate ( $\text{CaPO}_4$ ) present in the yeast extract and tryptone. Bottles included or did not include a cement piece to test its effect on the mineralization chemistry in solution.

Following inoculation with *G. thermodenitrificans* ( $\text{OD}_{600} = 0.20 - 0.30$ ) the pH of the medium decreased for the first 4 – 6 hours. Thereafter, the pH increased for 2 – 6 hours. This pH increase paralleled a decrease in calcium concentrations (Figure 1). No mineral precipitation was visible until 12-16 hours, following an approximately 30-40% decline in calcium concentration. The concentration of calcium declined more when cement was present than when it was not. This may be a result of the higher pH reached in this condition between the two treatments as higher pH favours the precipitation of minerals such as  $\text{CaCO}_3$ . In all inoculated treatments peak biomass (CFU/mL) was reached 2-4 hours before dissolved calcium levels began to drop (Figure 1). Also, carbonate analyses of dried minerals (pelleted and dried upon termination of the experiments) was performed according to the ASTM-D4373 and found  $\text{CaCO}_3$  yield in the range of 5-10%. Taken together, further experiments providing a second injection of fresh medium to the bacteria may help keep bacteria cell numbers high to produce more  $\text{CO}_2$  (via carbohydrate metabolism) and  $\text{OH}^-$  (via denitrification) and thus increase calcium precipitation. Also, it was observed by scanning electron microscopy of collected sediment that  $\text{CaPO}_4$  precipitated alongside  $\text{CaCO}_3$  which would reduce the  $\text{CaCO}_3$  yield. Further experiments to reduce the amount of phosphate in the biomineralization medium by reducing or replacing the yeast and tryptone could increase the amount of  $\text{CaCO}_3$  precipitated [8]. At present, lab work is underway to develop a chemically defined growth medium that reduces phosphate. Other analyte relationships were also found.

All treatments that included a cement piece had higher starting pH and dissolved analyte concentrations. This is presumably due to the leaching of cement minerals into the biomineralization

medium. Interestingly, sodium and phosphorous concentrations paralleled the decline of dissolved calcium. Thus, this suggests that measuring the levels of one analyte could be used to reliably predict the concentrations of other analytes in a biomineralization system. Additionally, nitrate was measured and found to decrease, in general from the start to end of a biomineralization experiment. Thus, the system remained anaerobic and denitrification had taken place.

Finally, microscopy on dried cement pieces revealed the precipitation of  $\text{CaCO}_3$ , alongside halite and  $\text{CaPO}_4$ , which demonstrates that the system could produce carbonate minerals on and around a cement surface. Thus, practically, this implies that MICP via denitrification has the potential to remediate leaky wells. The next phase of our research is to assess the efficacy of MICP with *G. thermodenitrificans* to determine how effective it is at reducing the permeability of fractured cement and porous rock samples in our wellbore analog system that will simulate repair operations at pressures and temperature expected at depth of up to approximately 4 km. We will also optimize treatment parameters (i.e., reducing phosphate concentrations).

## Novel/Additive Information

Overall there is evidence, from geochemical and microbiological data, for the use of bacterial denitrification to produce carbonate minerals (i.e.,  $\text{CaCO}_3$ ) as a means to repair annular leaks in wells at depths of greater than 1 km. This should be of immediate interest to the upstream oil and gas sector where wellbore leakage is a concern and for conditions in which conventional cement squeeze remediation is not effective. It should also be of interest for  $\text{CO}_2$  storage, for which well integrity is also a primary concern.

The long term durability of MICP-sealed leaks needs to be assessed. For example, it may not be suitable for formations that are lacking in calcium-bearing minerals due to the potential for the induced carbonates to dissolve. Its ability to tolerate fluctuating pressure and temperature conditions should also be assessed in order to determine if it is a suitable remediation method for wells undergoing stimulation (e.g., steam-assisted gravity drainage wells).

The extent and homogeneity of  $\text{CaCO}_3$  production in a sample, overtime, remains a concern for consistent repair. Finally, the results show that the concentrations of select species (i.e.,  $[\text{Ca}^{2+}]$ ) can be used as proxies for bacterial growth and  $\text{CaCO}_3$  formation for a known biomineralization system. This could assist sampling in field site testing where a single parameter could be used to estimate several others.

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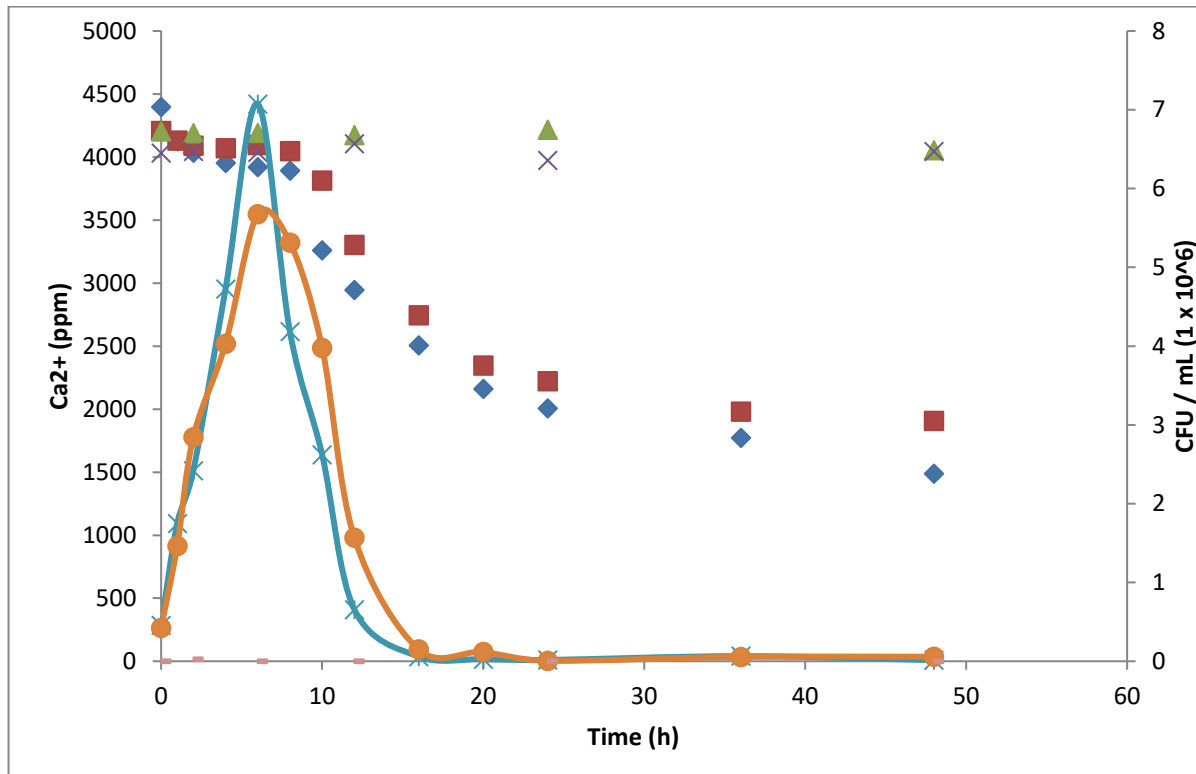


Figure 1: The change in soluble calcium ( $\text{Ca}^{2+}$ ) levels ( $n = 1$ ) and growth density ( $\text{CFU}/\text{mL}$ ,  $1 \times 10^6$ ) ( $n = 5 - 6$ ) as a function of time (h) for *G. thermodentrificans* in cementation medium (mLB, 10g/L  $\text{KNO}_3$ , 0.1M  $\text{Ca}^{2+}$ ) with or without a cement piece. Blue Diamond (Bacteria and cement) ; Red Square (Bacteria only) ; Green Triangle (Cement only) ; Purple X (Medium only) ; Blue line (Bacteria and cement) ; Orange line (Bacteria only)

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