Microbial Fluid-Rock Interactions in Chalk Samples and Salinity Factor in Divalent Ca^{2+} ions Release for Microbial Enhanced Oil Recovery Purposes

Ismaila A. Jimoh, Svetlana N. Rudyk and Erik G. Søgaard

Section for Chemical Engineering, Esbjerg Institute of Technology,
Aalborg University, Niels Bohr Vej 8, 6700 Denmark
egs@bio.aau.dk

In this study core laboratory experiments were performed on chalk samples from Danish sector of the North Sea to study microbial fluid-rock interactions with carbonate rock and to evaluate the dissolution of rock matrix ($CaCO_3$). The microbial media consisted of a strain of *Clostridium tyrobutyricum* with reinforced clostridia media and molasses as carbon and energy sources. Results showed that the average concentration of Ca^{2+} ions after microbial fluid interactions with chalk samples in media of salinity 40-100g/l increased from initial average concentration of 203 mg/l at the start of the experiment to 1178 mg/l in 28 days. All the bacteria media irrespective of their salinity condition experienced a decrease in measured pH from average of 7.0 to 6.0 in the first week; this however started to increase again from second week with release of calcium ions indicating a correlation between the pH and calcium ions released. 3-D surface plot for the range of salinity measured revealed delineation of the measured salinity into two groups with a boundary between 70 - 80 g/l. The highest Ca^{2+} ion concentration was measured at the highest salinities by the end of experiment which means that the dissolution rate of chalk increased with increase in salinity. This could be due to the lower values of pH as an indication of that higher salt concentration facilitates more acid production by bacteria.

1. Introduction

Microbial fluid interaction in subsurface formations is governed by complicated physical, chemical, and biological phenomenon. Although several attempts have been made to describe microbial processes, no model has yet fully incorporated all of the complex phenomena that are believed to be important thus it requires close coordination between laboratory mechanistic studies and oil displacement experiments under carefully controlled conditions to develop and validate a computer model (Bryant et al., 1992). Development of such models must incorporate all the physical, chemical and biological processes that occurres during microbial enhanced oil recovery (MEOR) processes such as adsorption, interaction between microorganisms and substrate, biomass formation and ions release. Many works have been carried out to document different aspect of MEOR processes; however the release of divalent Ca^{2+} ions and the role played by the reservoir brine remains one of the least studied parts of microbial

fluid rock interaction during microbial enhanced oil recovery. Only few reports refer to ions release during MEOR process in carbonate rocks. During microbial fluid interactions with carbonate rocks, divalent cations are being released as a consequence of dissolution of the rock matrix (Udegbunam et al, 1991). Adkins et al., 1992b have reported similar phenomenon in their work where they used a halophilic bacteria in-situ growth in a packed columns with crushed carbonate rocks. However, they did not mention the concentration of Ca^{2+} ions released. Divalent cations such as Ca^{2+} can influence biofilm formation and can possibly enhance adhesion of bacteria to the rock particles in the medium (Marshall, 1985). In microbial enhanced oil mechanism, migration of these adhered bacteria to other parts of the reservoir rock can induce mobilization of oil in the new location.

In the present study, we describe the microbial fluid interaction with chalk samples at different salinity and the release of calcium ions from this interaction. Incorporation of such information can increase our understanding of models that attempts to describe fluid-rock interaction during microbial enhanced oil recovery.

2. Experimental Procedure

The chalk samples used in this investigation were obtained from Dan-chalk. These chalk samples were cut into identical cylindrical shapes of 2.0 cm length and 2.4 cm diameter. They were characterized by whitish, fine textured and average porosity of 40%. The chalk samples were pre-treated by drying in the oven for 72 hours at 90 °C. The method of modification involved immersion of the chalk samples in growth chamber filled with microbial solution at different salinity. The salinity range used in the experiment was 40 -100 g/l. (4-10 % w/v). The growth chambers were 500 ml fermentation bottles with cork consisting of a hole for sample withdrawal. The bottles were autoclaved at 121 °C for 20 minutes. A sterile oxygen free stream of nitrogen was passed through the flask for 15 minutes to create oxygen free environment. Sodium chloride salt of different concentration was dissolved in 250 ml of de-ionized water to provide the desired values of salinity.20 ml of molasses was then added to each flask to serve as source of nutrient. The medium were inoculated each with 10 ml of a strain of *Clostridium tyrobutyricum* designated as 90F. This strain was already adapted to grow till salinity range of 100 g/l. Detail of the adaptation process is given in (Rudyk and Søgaard, 2010). The bacteria had earlier been cultivated on a reinforced clostridia media (RCM). The whole set up for main experiments and control experiments (without chalk samples) and blank experiments (chalk and salt solutions only) to check background values were incubated at 37 °C for 28 days under anaerobic condition. Growth in the media was indicated by increased turbidity. The pH and electrical conductivity measurements were made every 7 days and the fluid samples analyzed for calcium ions concentration by induction couple plasma (ICP).

3. Results and Discussion

Fig.1. shows the relationship between Ca^{2+} concentrations with time. A significant content of Ca^{2+} was found for all the media and this correlates with the period of

immersion. The average concentration at 7, 14, 21, and 28 days for the salinity measured was 611, 822, 2100 and 3257 mg/l, respectively. This amount is significantly different when compared to the average value of 203 mg/l for control experiment (the average starting point of all salinity measured without chalk samples) and average background value of about 50 mg/l for blank experiment (chalk samples and salt solutions at 90 g/l) over the same period of time. However, correlation between the Ca^{2+} ion content in the fluid and salt concentration cannot be ascertained as it was hardly seen on day 7 and 14 and became very irregular on day 21 and 28.
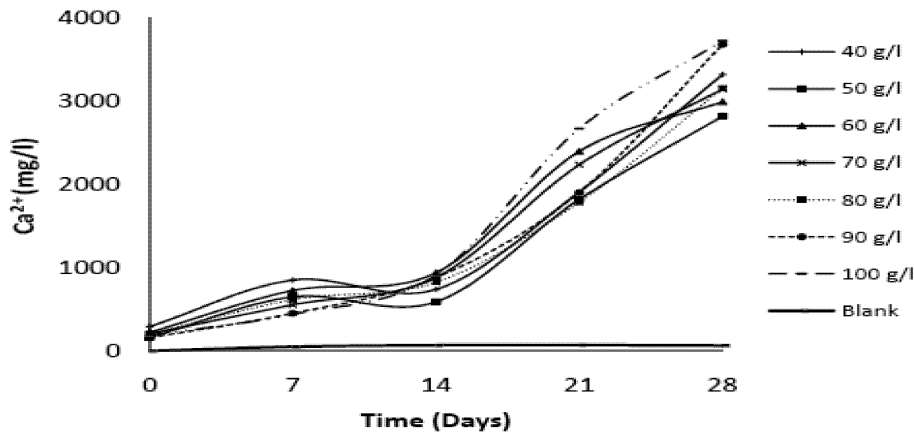

Figure 1. Ca^{2+} ions concentration variation with time at different salinity
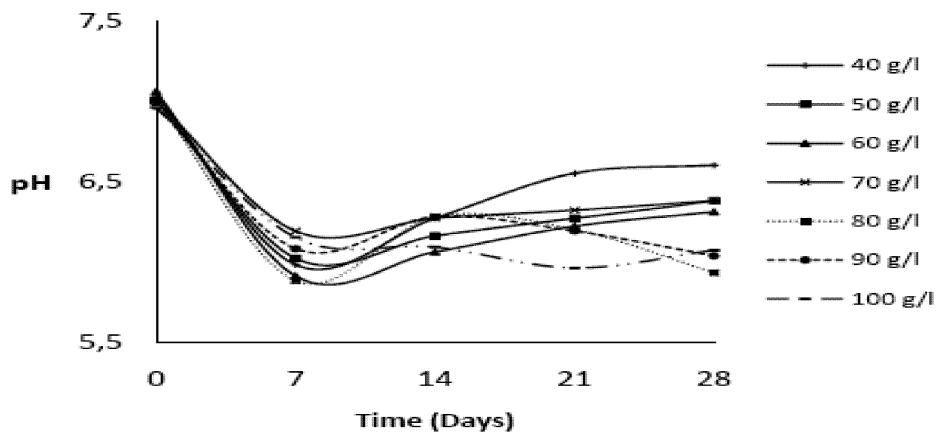

Figure 2. pH variation with time at different salinity

The change in pH of the media with time is shown in Fig.2. For salinity 40, 50, 60 and 70 g/l, the pH is increasing from day 7 to the end of 28 days, while for salinity 80, 90 and 100 g/l the pH is decreasing from day 14 suggesting more acidic condition. These

results appeared to separate the salinity range into two groups i.e. 40, 50, 60, and 70 g/l and 80, 90 and 100 g/l. Increase in the pH of the media with time is indicative of carbonate mineral dissolution as represented by equation (1). This will lead to formation of water soluble bicarbonates.

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^{2-} \tag{1}$$

As the concentration of HCO_3^{2-} increases, the media become less acidic and the pH increases. The opposite effect noticed at salinity (80 -100g/l) from day 14 which is more acidic can be attributed to effect of salinity on metabolism of bacteria that promotes more acid production and reduces the influence of HCO_3^{2-} on pH.
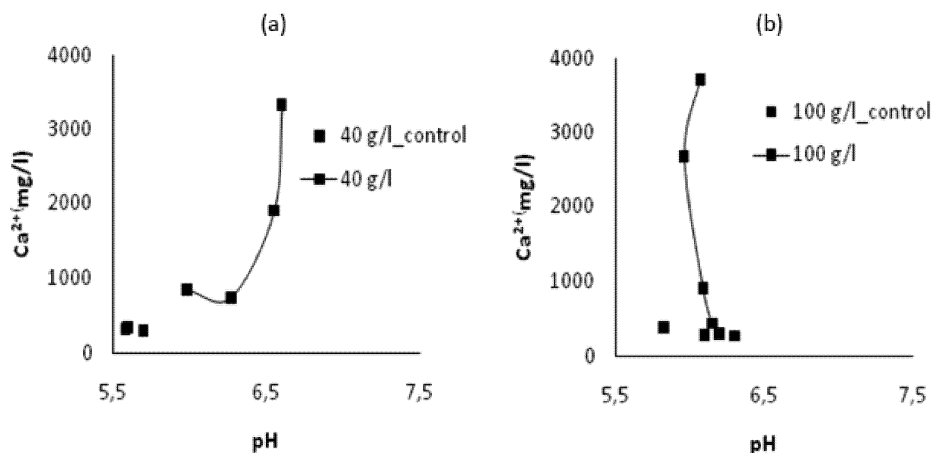

Figure 3.Comparison of media dynamics at (a) 40 g/l and (b) 100 g/l

The dynamics of the media with chalk samples were compared with those of control experiments without chalk samples at different salinity for example 40 and 100 g/l as shown in Figure 3. The results for all salinity measured put together is shown in Fig 4. A strong correlation can be observed between pH and Ca^{2+} concentration with time for the measured salinity range (Fig.4). The equations show a negative correlation for different period of time and an almost equal gradient for dissolution of Ca^{2+} ions which is reflected in parallel lines and almost equal constants in equations. The system is limited with lines between 40 and 100 g/l showing that low salinity corresponds to high pH and high salinity corresponds to low pH. This negative correlation can be an indication of increasing acidic environment with increasing salinity despite relatively higher concentration of Ca^{2+} ions. For more clear presentation of this multivariate system, 3D surface model was made as shown in Fig.5.
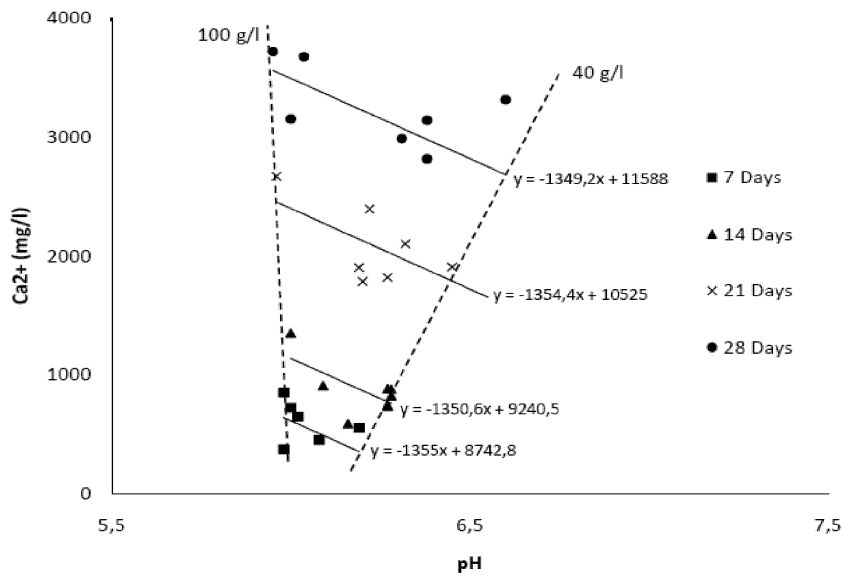
Figure 4.Overall dynamics of the media based on Ca^{2+} ions concentration and pH
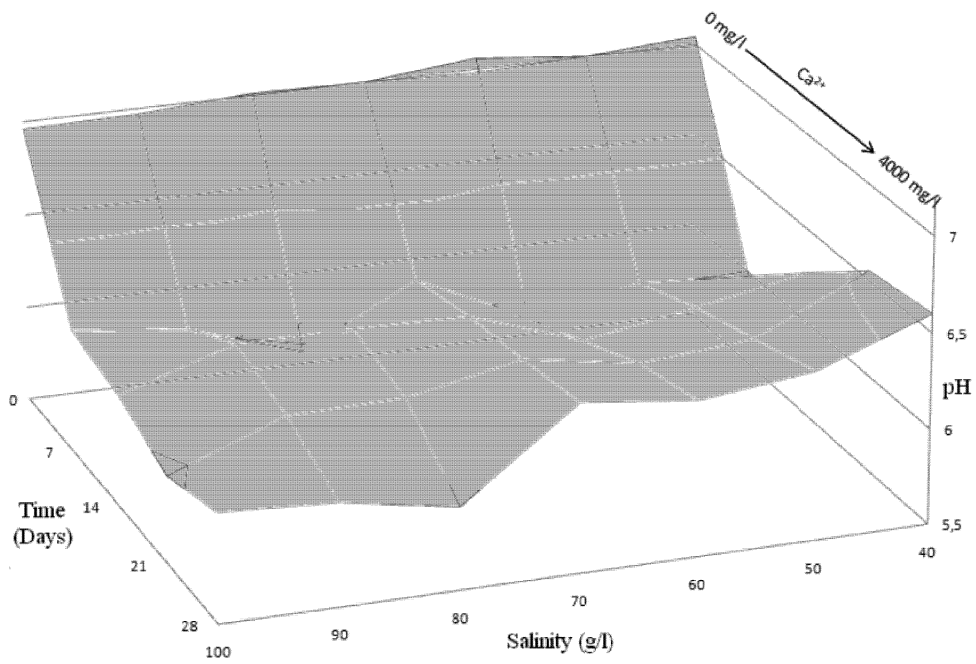

Figure 5. Surface representation of the media parameters

3-D surface plot for all the media (i.e. 40 -100 g/l) as shown in Figure 5 revealed an interesting result. The plane angle of the salinity measured was delineated into two with a boundary between 70-80 g/l that separates the low salinity group (40, 50, 60 and 70 g/l) and high salinity group (80, 90 and 100 g/l). The low salinity group has an elevated plane surface corresponding to higher pH while the high salinity group has a lower plane surface that corresponds to lower pH than the low salinity group. The model thus confirms the deviations corresponding to the low salinity and high salinity groups. These deviations could be related to the effect of different rates of metabolic process of the bacteria in the different ranges of salinity. At high salinities, the condition in the medium was slightly more acidic. It is also likely that a part of pH change comes from salinity alone and the resultant change in activity coefficients. The pH of aqueous sodium chloride was found to vary with increasing salinity due to different ionic strength (unpublished results).

4. Conclusion

The results from this study suggest that incongruent dissolution of chalk samples by microbial solution at different salinity enriched the solution with Ca^{2+} ions about 20 times more than the background value. However, the concentration of Ca^{2+} ions in the media did not have clear correlation with salinity. The highest release of Ca^{2+} ions due to higher acidity was observed at harsher environment for bacteria at the highest salinity. The 3-D surface plot was able to distinguish a possible partitioning of pH along two salinity groups. This effect on pH is clearly related to the concentration of Ca^{2+} ions in the media over time due to bacteria metabolism or those coming from salinity alone. These parameters should be taken into consideration when modeling for microbial fluid rock interactions in carbonate rocks.

References

Adkins J.P., Tanner R.S., Udegbunam E.O., McInerney M.J. and Knapp R.M., 1992b,Microbially enhanced oil recovery from unconsolidated limestone cores,Geomicrobiol. J. 10, 77-86.
Bryant R.S., Bertus K.M., Stepp A.K., Chang M. and Chase K.L., 1992, Laboratory studies of the parameters involved in modeling microbial oil mobilization, SPE/DOE enhanced oil recovery symposium, 22-24 April, Tusla, Okl., USA.
Marshall K.C., 1985, Bacterial adhesion mechanisms and physiological significance: Mechanisms of bacterial adhesion at solid-water interfaces, Eds. Savage D.L. and Fletcher M., Plenum, New York, 133-157.
Rudyk S. and Søgaard E., 2010, Applied microbiology and molecular biology in oilfield systems: Microbial enhanced oil recovery, Eds. Whitby C. and Skovhus T.L., Springer, Dordrecht, 179-187.
Udegbunam E.O., Adkins J.P., Knapp R.M. and McInerney M.J., 1991, Assessing the effects of microbial metabolism and metabolites on reservoir pore structure,SPE22846, Proceedings of SPE annual technical conference and exhibition,Society of Petroleum Engineers, Richardson, Texas.