

Modeling Chemical Evolution of Cement Seals

Hugh Shortt

Mickey Leland Energy Fellow Summer Internship Summary Paper

August 2017

Abstract:

The prevention of the migration of fluids is a field of study with high demand in both the private industry as well as in government research and development. More particularly, the prevention of carbon dioxide (CO₂) migration or return to the atmosphere. This, in turn, causes measurably significant atmospheric climate change that results in immense damage to the environment.

In this study, the interaction between 0.5 molar sodium chloride (NaCl) brine solution and a cement interface over extended periods of time is computationally investigated, as well as the interaction of a 33 millimolar CO₂ dissolved in the afore-mentioned brine solution for the same period of time. A 2-meter-long saturated brine solution reacted with an 800-meter-long cement block in PFLOTTRAN, an open-source reactive flow transport software whose output was later visualized in ParaView, a separate, open-source, visualization software.

The effects of the chemo evolution of brine with cement is studied in detail. It has been reported that the solidified products could potentially exacerbate pre-existing microannuli in the cement-casing interface through which CO₂ can migrate and therefore, return to the surface atmosphere. Thus, it is of vital importance to predict the behavior of cement used for intersecting a CO₂ storage site.

Introduction:

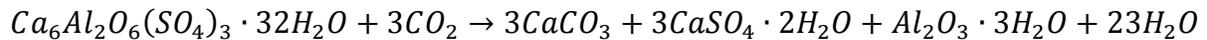
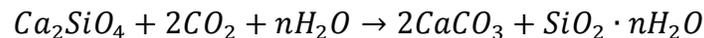
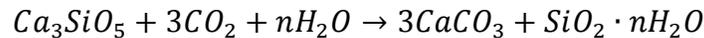
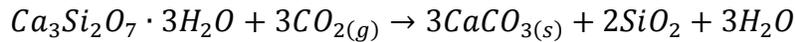
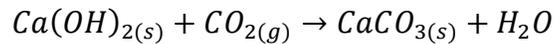
Cement seals are vital for the isolation of fluids from a body of interest. When fluids such as CO₂ react with the cement seal over an extended period of time and produce other solid products resulting in the development of leakage pathways within the wellbore. These leakage pathways allow the migration of CO₂ from the zone of isolation back to the surface for re-entry into the atmosphere. In this study, the chemical interaction of CO₂ with Portland cement is investigated most heavily.

There are several experimental and computational studies on cement reaction with CO₂ (Zhang et. al, 2011). The published models can be divided into two large groups: macroscopic and microscopic models. Macroscopic models do not easily show the pore scale dynamics of filtration or the clogging of pores as a result of infiltration in minute detail, however, do hope to capture larger trends. Microscopic models on the other hand, are meant to model pore scale geometry and are capable of incorporating complex details of the transport and deposition processes. Nevertheless, exact theory for interaction of particles and pore-grain surface of general shape is not yet known, and as a result, are assumed to be spherical particles and locally straight interfaces. For the purposes of this study, a macroscopic model was used to

investigate the behavior of Portland cement that has been exposed to a 0.5 Molar NaCl Brine solution as well as a 0.5 Molar NaCl Brine solution with 33 milli Molar carbon dioxide (CO₂) dissolved in it (i.e. a brine solution saturated with CO₂).

Portland cement clinker is made up primarily of four phases: tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$), tricalcium aluminate ($Ca_3Al_2O_6$), dicalcium silicate (Ca_2SiO_4), and tricalcium silicate (Ca_3SiO_5) (Taylor, 1997). Gypsum is typically added during the production of Portland cement. As a result of the vast range of subsurface conditions, upwards of 100 cement additives such as accelerators, retarders, extenders, weighing agents, and fluid-loss control agents that have previously been developed to allow Portland cement to survive these subsurface conditions. (Michaux et al., 1989).

Cement carbonation is a phenomenon that occurs when cement is exposed to and chemically attacked by CO₂. The process of cement carbonation requires the reaction of CO₂ with calcium and hydroxyl ions that are located in the pore water of cement paste to produce calcium carbonate. Some examples of other hydration products of Portland cement that are prone to carbonation in the presence of fluids include, but are not limited to: $Ca(OH)_2$, $Ca_3Si_2O_7$, Ca_3SiO_5 , Ca_2SiO_4 , and $Ca_6Al_2O_6(SO_4)_3$. (Groves et al., 1991) observed the progression of carbonation in C_3S pastes that were exposed to and left to react with pure CO₂ for several hours. It was reported that calcium was gradually leached from the calcium silicate hydrate (CSH) present in the cement and was able to detect a decrease in the Ca/Si ratio. The overall chemical reaction for each hydration product is as follows (Zhang et al. 2011):



It is, however, also important to note that when the hydration phases react with CO₂, water is produced. The reason why this is important to note is that the produced excess water (pore water) blocks the cement pores which significantly hinders the diffusion of CO₂ through the pores, and as a consequence, retards the rate of calcium carbonation (Richardson, 1988). It was, however, experimentally found that the other opposing extreme would produce similar results given that some water is required to catalyze the reaction. In other words, samples subjected to extreme drying conditions also carbonated very slowly (Reardon et al. 1989). One of the most important factors that impacts the physical and chemical properties of cement pastes is the rate of carbonation. The rate of carbonation is dependent on a number of factors such as cement type, water/cement ratio, additives, temperature, CO₂ concentration, relative humidity, and curing conditions. The impact on the affected chemical and physical properties

include the amount of calcium hydroxide present in the cement paste, as well as the porosity and permeability thereof.

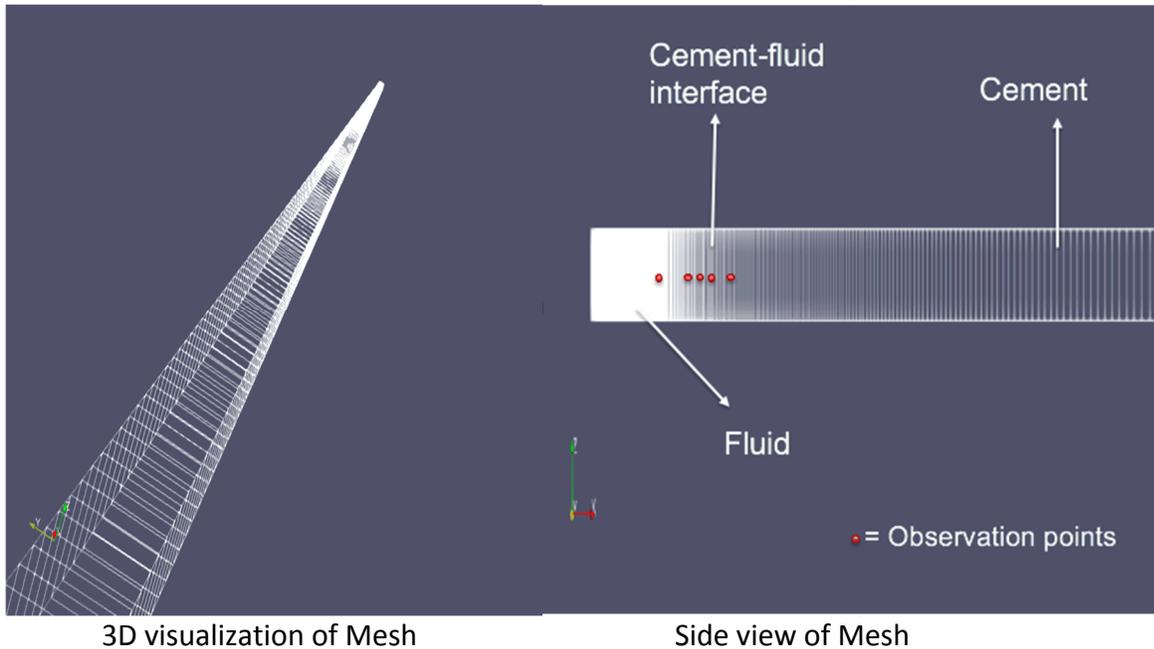
In sum, Portland cement clinker is made up primarily of four phases: tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$), tricalcium aluminate ($Ca_3Al_2O_6$), dicalcium silicate (Ca_2SiO_4), and tricalcium silicate (Ca_3SiO_5). The products formed after the reaction between calcium silicates and water include portlandite and CSH. Calcium carbonate is the primary carbonation product, the composition of CSH changes with the progression of carbonation which is controlled by a diffusion –dominant process. Calcium is slowly leached out of CSH. And the rate of carbonation is determined by factors such as cement type, water/cement ratio, additives, temperature, CO_2 concentration, relative humidity, and curing conditions (Zhang et al. 2011).

Methods:

To begin, the following was assumed for the initial problem set up: First, the constant boundary condition was assumed in the fluid reservoir with a one atmosphere CO_2 pressure head. This was assumed so that when the fluid was allowed to computationally react with the cement seal for a long period of time, there would be an infinite CO_2 sink and hence, the CO_2 in the fluid would not become the limiting reagent. Second, the cement seal was assumed to be an ordinary Portland cement (OPC) plug. The reason for this was because the choice for cement in wellbore use is typically a cement that is commonly available. Among these, one of the most commonly used cement types is Portland cement. Third, a one dimensional square mesh was used for the purpose of more easily analyzing the system at a macroscopic scale. The primary area of interest involved the interface of the fluid and cement, so that the overall behavior between the fluid and cement interaction can be better observed.

For the purposes of understanding how the presence of CO_2 affects the chemical evolution at the cement-fluid interface, two cases were run: For the first case, it was assumed that the 0.5 Molar NaCl brine solution was free of any CO_2 . This allowed for the observation of the brine-cement interaction strictly. In the second case, 33 milli Molar CO_2 was dissolved into the same 0.5 Molar NaCl brine solution to analyze the differences in leaching and carbonation products due to CO_2 attack.

The aforementioned model was implemented in the PFLOTRAN reactive transport code. The mesh dimensions were set so that the measured length of the brine solution would be two meters, followed by over 800 meters of Portland cement to model a semi-infinite domain. Within the mesh, five observation points were set at the following coordinates: (1.00 m, 2.5 m, 2.5 m), (1.99 m, 2.5 m, 2.5 m), (1.8 m, 2.5 m, 2.5 m), (2.00 m, 2.5 m, 2.5 m), and (2.3 m, 2.5 m, 2.5 m) respectively.

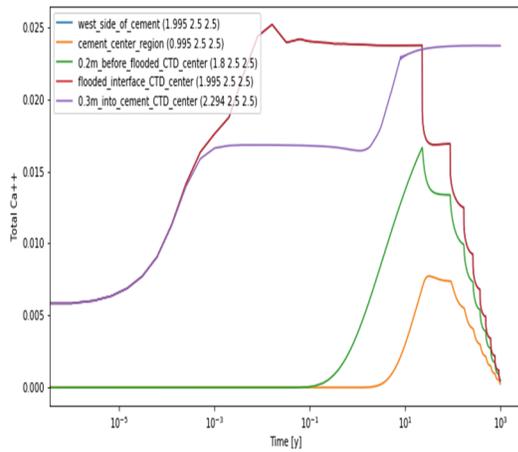


PFLOTRAN is an open source, state-of-the-art massively parallel subsurface flow and reactive transport code. PFLOTRAN solves a system of generally nonlinear partial differential equations describing multiphase, multicomponent and multiscale reactive flow and transport in porous materials. The code is designed to run on massively parallel computing architectures as well as workstations and laptops. Parallelization is achieved through domain decomposition using the [PETSc](#) (Portable Extensible Toolkit for Scientific Computation) libraries. PFLOTRAN has been developed from the ground up for parallel scalability and has been run on up to 2^{18} processor cores with problem sizes up to 2 billion degrees of freedom. PFLOTRAN is written in object oriented, free formatted Fortran 2003. The choice of Fortran over C/C++ was based primarily on the need to enlist and preserve tight collaboration with experienced domain scientists, without which PFLOTRAN's sophisticated process models would not exist. The reactive transport equations can be solved using either a fully implicit Newton-Raphson algorithm or the less robust operator splitting method. (Hammond et al. 2014)

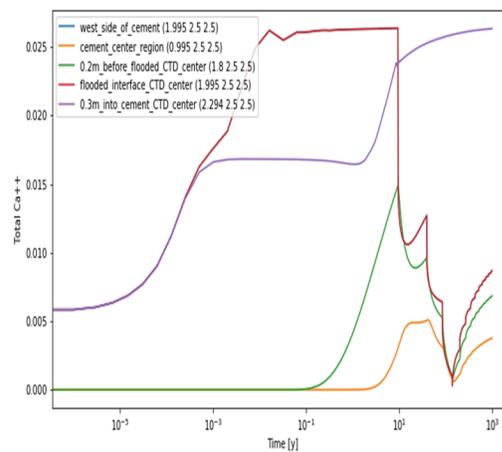
The Operating Hypothesis for the purpose of this study is where brine with CO_2 dissolved in it is expected to dissolve and/or chemically damage the cement faster between the two cases since the CO_2 saturated brine is acidic in nature.

Results and Discussion:

Below are the observed results for total change in calcium:



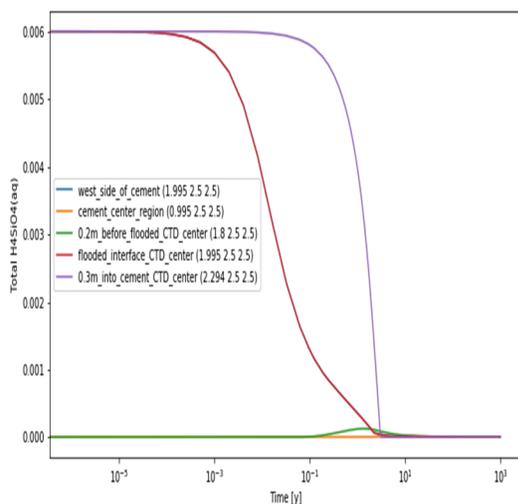
Total change in Ca⁺⁺ without CO₂ (log scale)



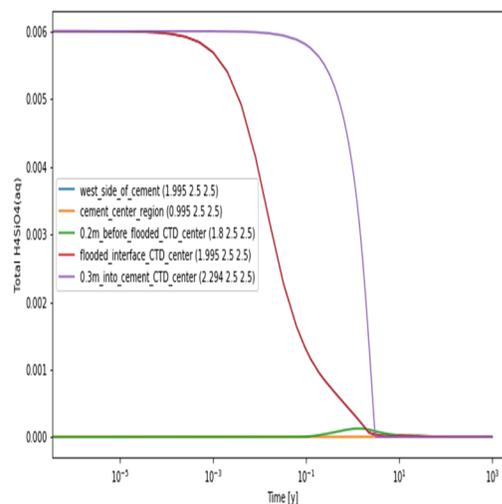
Total change in Ca⁺⁺ with CO₂ (log scale)

As seen above, the fluid-cement interface undergoes an increase in total calcium present. This would indicate that carbonation is observed at the fluid-cement interface and other carbonation products can be expected as a result. Of note, it is also interesting to see how as time increases, the presence of CO₂ causes a faster rate of decrease in total calcium observed in most observed regions, until approximately 100 years where the total calcium observed in the system begins to return. It is suspected that this is due to the precipitation of solid precipitates during the cement carbonation process.

Below are the observed results for Total H₄SiO₄ (aq):



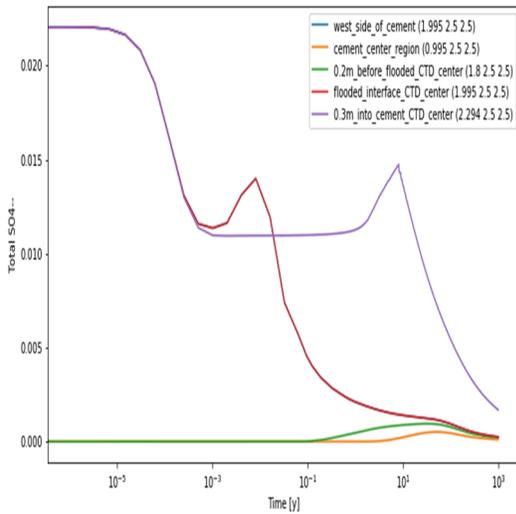
Total H₄SiO₄ (aq) change without CO₂ (log scale)



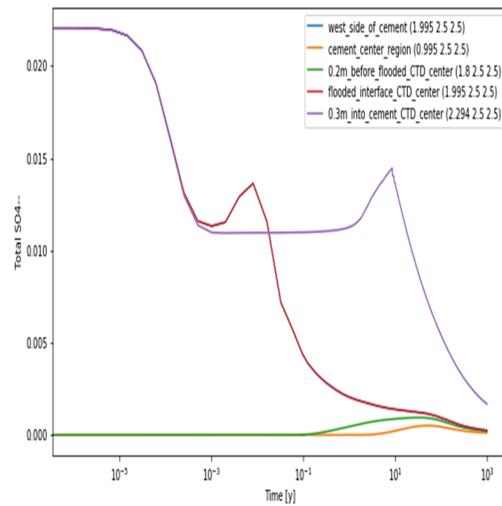
Total H₄SiO₄ (aq) change with CO₂ (log scale)

In the results for *Total H₄SiO₄ (aq)*, it was observed that the total change over 1000 years in both systems did not undergo any significant observable change in the presence of CO₂. It is known that since CO₂ is acidic in nature, the overall pH level in the system would change as a result. This observation was expected since *H₄SiO₄ (aq)* is not known for being very sensitive to changes in the level of pH present in the system.

Below are the observed results for total SO₄:



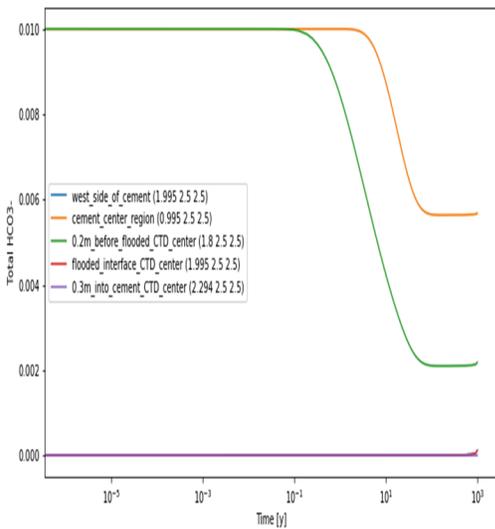
Total SO₄ change without CO₂ (log scale)



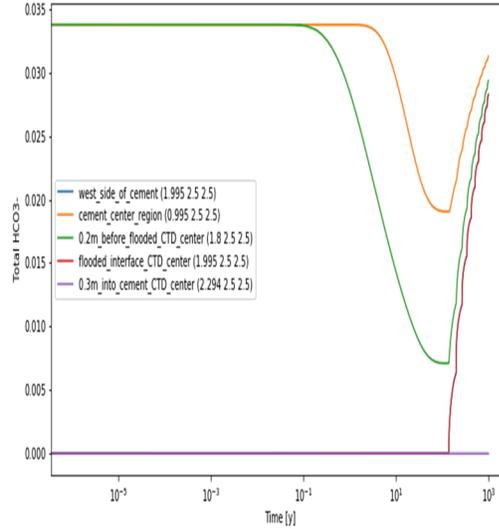
Total SO₄ change with CO₂ (log scale)

In the results for *Total SO₄*, it was also observed that the total change over 1000 years in both systems did not undergo any significant observable change in the presence of CO₂. This observation was expected since *SO₄* is not known either for its sensitivity to changes in the level of pH present in the system.

Below are the observed results for *Total HCO₃*:



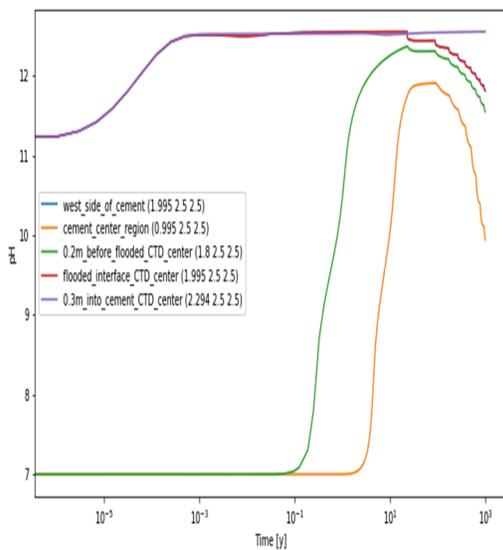
Total HCO₃ change without CO₂



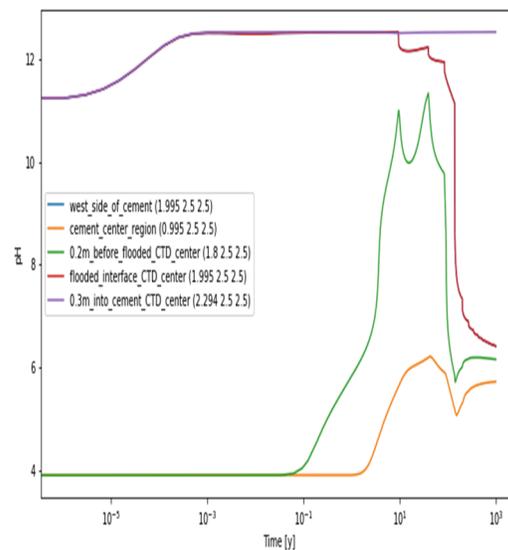
Total HCO₃ change with CO₂

It is important to note that the total change in HCO₃ maps with carbonate speciation via pH. The published knowledge of the relationship between the total change in HCO₃ and the total change in pH in the system states that they are inversely proportional to each other. The erratic increase in the *Total HCO₃* in the system is suspected to be due to the precipitation of solid precipitates during the carbonation process.

Total pH change without CO₂ vs. with CO₂ on log scale maps with the carbonate speciation:

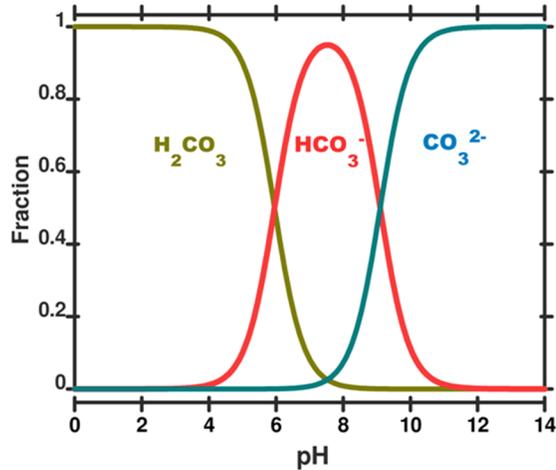


Total pH change without CO₂ (log scale)



Total pH change with CO₂ (log scale)

As previously noted in the results for the change in HCO_3^- , total change in pH level can be seen above where both pH and HCO_3^- are inversely proportional to each other regardless of the presence of CO_2 or not. The erratic descent in the level of total pH in the system is suspected to be due to the precipitation of solid precipitates during the carbonation process.



Published Graph of Carbonation via pH mapping

Summary and Conclusions:

In summary, the results for Total SO_4 and H_4SiO_4 did not change significantly with the continued exposure to dissolved CO_2 in the 0.5 Molar NaCl Brine solution. There was an increase of total calcium observed at the cement-fluid interface due to carbonation. Lastly, total change in HCO_3^- observed and total level of pH observed in the system are inversely proportional to each other, which is a clear reflection of the carbonate speciation dependency on pH.

Acknowledgements

Special Thanks to Dr. Ed Matteo, Dr. Jové-Colón, Dr. Kristopher Kuhlman and Robert Barnes.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. SAND2017-xxxx

References Cited:

Groves, G.W., Brough, A., Richardson, I.G., Dobson, C.M., 1991. *Progressive changes in the structure of hardened C₃S cement paste due to carbonation*. Journal of American Ceramic Society 74(11), 2891-2896.

Hammond, G.E., P.C. Lichtner and R.T. Mills, 2014. Evaluating the Performance of Parallel Subsurface Simulators: An Illustrative Example with PFLOTRAN, Water Resources Research, 50, doi:10.1002/2012WR013483.

Michaux, M., Nelson, E., Vidick, B., 1989. *Cement Chemistry and additives*. Oilfield Review 1 (1), 18-25.

Reardon, E.J., B.R., Abouchar, J., 1989. *High Pressure carbonation of cementitious grout*. Cement & Concrete Research 19, 385-399.

Richardson, M.G., 1988. *Carbonation of Reinforced Concrete: Its Causes and Management*. Citis Ltd., Dublin, London and New York.

Taylor, H.F.W., 1997. *Cement Chemistry*, 2nd ed. Academic Press, New York.

Zhang, M. and S. Bachu, 2011, *Review of integrity of existing wells in relation to CO₂ geological storage: What do we know?* SPE J. 826-840.

References Consulted:

Feng, Y. and K. E. Gray, 2016, *A fracture-mechanics-based model for wellbore strengthening applications*, SPE J. 392-400.

Pabalan, R.T., F.P. Glasser, D.A. Pickett, G.R. Walter, S. Biswas, M. R. Juckett, L.M. Sabido, and J.L. Myers, 2009. *Review of Literature and Assessment of factors relevant to Performance of Grouted Systems*

Rutqvist, J., L. Blanco-Martin, J. Birkholzer, 2016, *Use of a Dual-Structure Constitutive Model for Predicting the Long-Term Behavior of an Expansive Clay Buffer in a Nuclear Waste Repository*, Int. J. Geomech., 16(6).

Xiaoyan S., J. Holder, K.E. Gray, D. DiCarlo, 2013, *Coupled solid and fluid mechanics modeling of formation damage near wellbore*. SPE J. 88-96.