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Calcite Dissolution in Geothermal Reservoirs Using Chelants

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Keywords

chelants, EDTA, NTA, calcite, reactive-transport modeling, chemical stimulation

ABSTRACT

Chemical stimulation was studied in the laboratory as an alternative to hydraulic stimulation for increasing well injectivity and near-wellbore permeability in geothermal reservoirs. Two chelants, EDTA and NTA, were investigated for use as mineral-dissolution agents. A laboratory reactor was designed and fabricated for simulating the dissolution of calcium carbonate using these and other dissolution agents under controlled conditions that simulate a geothermal reservoir. Preliminary experimental data indicate that both EDTA and NTA are effective dissolution agents and that dissolution capacity increases with temperature. A reactive transport model of the laboratory reactor was constructed using TOUGHREACT for the purpose of simulating the calcite-dissolution process. Initial results indicate that, as expected, dissolution rate is directly proportional to flow rate, but indirectly proportional to pH.

Introduction

Geothermal wells are occasionally drilled into formations in which the fractures contain considerable amounts of calcite, decreasing fracture permeability. Likewise, fluids within geothermal production wells often become oversaturated with calcium carbonate, resulting in calcite and/or aragonite deposition and the concomitant plugging of wellbores or near-wellbore formations. Scale-inhibition treatments through the continuous injection of scale-inhibitor chemicals via capillary tubing have been shown to prevent the deposition of calcite within wellbores, but such treatments have no effect on the near-wellbore formation. Therefore, in reservoirs that are severely drawn down fluids boil in the near-wellbore formation and deposit calcite.

Currently the two leading approaches for the removal of calcite from wellbores are mechanical cleaning and acid

treatment. Mechanical cleaning involves the reaming of the wellbore, followed by flowing the well to remove debris. Such a procedure may not always be an option due to casing damage and/or the presence of tubing or other obstacles in the wellbore.

An option to mechanical cleaning, chemical treatment of the wellbore and of near-wellbore formations is commonly accomplished by injecting strong mineral acid treatments from the wellhead. At high geothermal temperatures, however, mineral acids risk corroding steel casings. Acids injected from the surface also tend to enter the formation via the first fluid entry zone, dissolving first-contacted minerals aggressively while leaving much of the rest of wellbore untreated. Whereas steel casings can usually be protected during acid stimulation by using corrosion inhibitors (except at temperatures approaching or exceeding 300°C), controlling the reactivity of the strong mineral acid towards calcite dissolution is a more challenging problem.

An alternative to acid treatment is the use of chelating agents such as ethylenediaminetetraacetic acid (EDTA) or nitrilotriacetic acid (NTA). Such chelating agents have the ability to chelate, or bind, metals such as calcium. Through the process of chelation, a calcium ion would be solvated by the chelating agent, allowing the calcite to be transported either to the surface by flowing the well or further into the formation

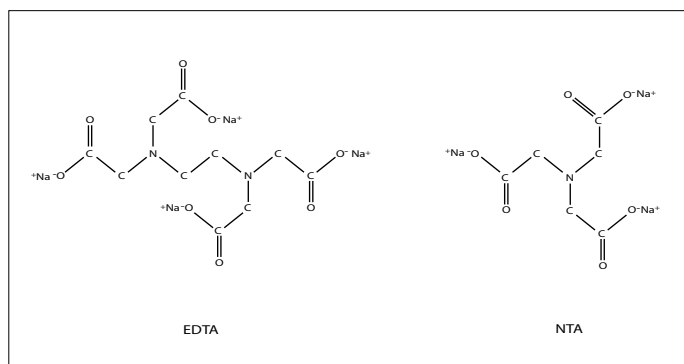


Figure 1. Chemical structures of the sodium salts of EDTA and NTA.

by injecting into the well. The rate of calcite dissolution using chelating agents is not as fast as is the rate of calcite dissolution using strong mineral acids. The lower dissolution rate means that the chelating agent will be able to take a more balanced path through the wellbore and more evenly dissolve calcite in all available fractures, rather than following the first fluid entry zone and leaving the rest relatively untouched.

Chelating Agents

The structures of the two chelating agents in anionic form are shown in Figure 1.

In the calcite chelating process, one EDTA molecule will associate with two Ca^{2+} ions, therefore allowing theoretically for the dissolution of 2 moles of calcite per mole of EDTA. Likewise, two NTA molecules are required to dissolve 3 calcite molecules.

Experimental Procedure

In order to study the in situ dissolution of calcite, a high temperature laboratory flow reactor was designed and fabricated. The reactor system required a high pressure/temperature reaction vessel, a heat source, a high-pressure pump, a cooling system, and a sample chamber. Figure 2 shows the design of the dissolution reactor. The completed reactor is seen in the photograph in Figure 3.

In a typical experiment, the candidate dissolution agent was dissolved at an appropriate concentration and the solution was sparged with helium, removing any dissolved gasses. The candidate solution was pumped into the preheater using a Waters 600E HPLC pump and system controller. The fluid then entered the temperature-controlled dissolution chamber at the target temperature where it contacted the mineral sample. The

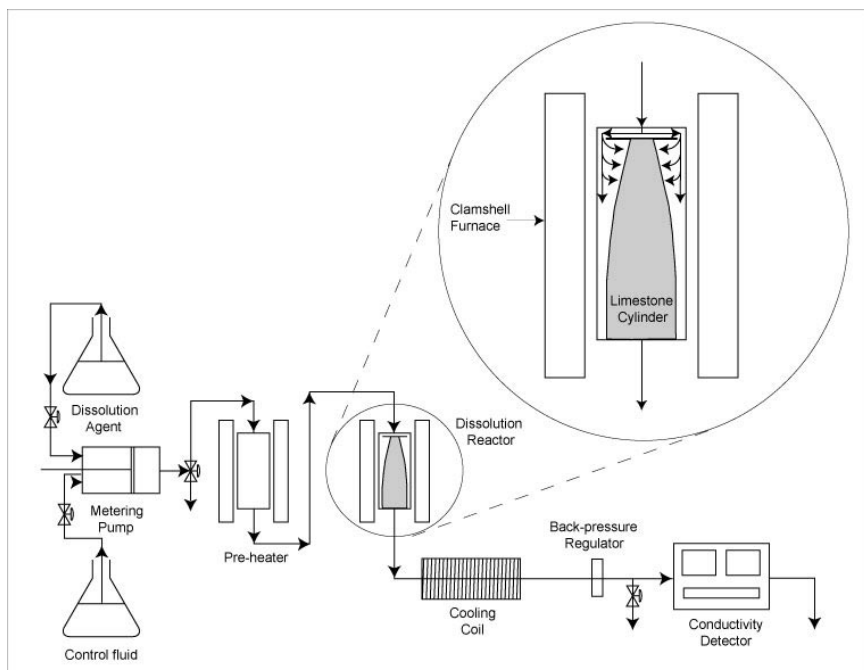


Figure 2. Schematic of the mineral dissolution reactor.

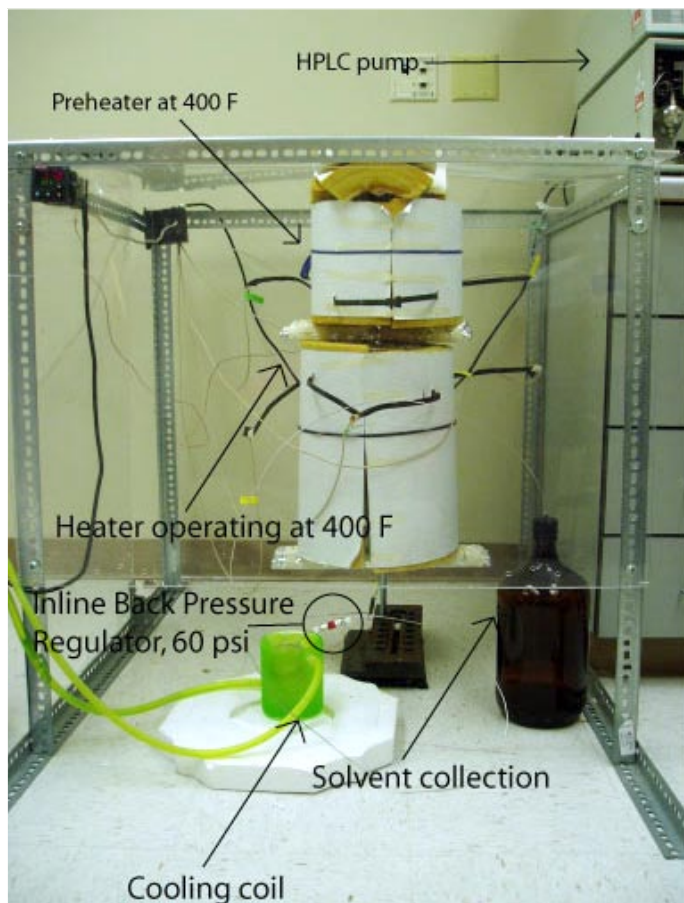


Figure 3. A photograph of the mineral dissolution reactor.

heated solution was allowed to flow over the sample, allowing for sufficient contact time to dissolve a quantifiable mass. After exiting the dissolution chamber, the fluid then flowed through a cooling coil. A back-pressure regulator allowed for controlled flow to the solvent collector. Discrete samples were taken from the solvent collector and analyzed using a Waters 431 conductivity detector. The mineral sample consisted of limestone rods 2.48 cm in diameter and approximately 15 cm long, cut from a slab of Texas Limestone using a coring bit.

In order to ensure reproducibility, a procedure was developed for handling the limestone sample cylinders before and after subjecting them to the dissolution experiments. Initially, each limestone sample was dried for a minimum of 2 hours in a drying oven at 110°C before being weighed. At the completion of each run the core was removed from the reactor and rinsed with DI water. The core was then placed in the drying oven for a minimum of 2 hours and then removed and weighed again in order to calculate the dissolved mass.

Figure 4 shows graphically initial and preliminary results for the mass dissolved per volume flowed as a function of temperature for solutions of the chelating agents EDTA and NTA at pH 7.

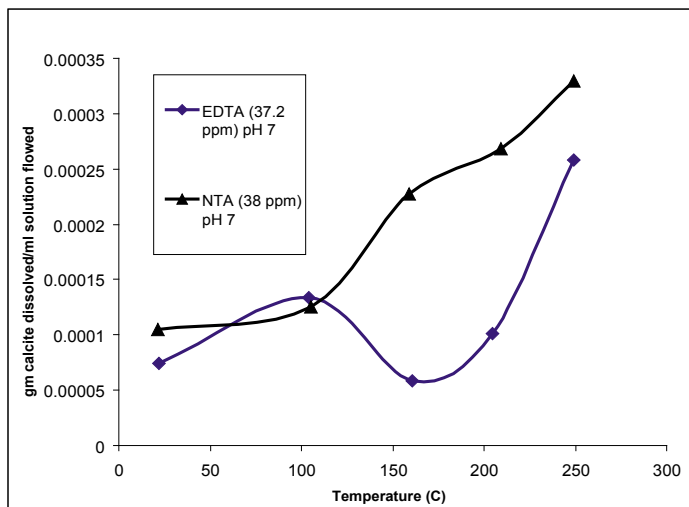


Figure 4. A plot showing the mass of core dissolved per volume of solvent flowed at various temperatures for the two chelating reagents.

The trend of increasing dissolution with increasing temperature for both chelating reagents is reasonable. However, the apparent decrease in dissolution between 100 °C and 200°C for EDTA cannot be explained. Experiments are continuing in an effort to establish reaction conditions that produce consistent results.

Reactive Transport Modeling

Reactive transport models are powerful tools for simulating the mineral dissolution processes of fluids flowing through fractured rock in geothermal formations. Such models can likewise be used to simulate dissolution processes in laboratory reactors, which, themselves, serve to model reactive transport processes in geothermal reservoirs. The objective of this task is to simulate the mineral dissolution/precipitation processes within the above-described laboratory reactor using the reactive transport code TOUGHREACT (Xu and Pruess, 1998, 2001).

Using reaction equilibria and kinetics data, simple 1-D models were constructed to model the laboratory reactions under various conditions. The experimental data can then be compared to the model outputs and the model will be calibrated as necessary. The calibrated models can themselves be used to construct reactive transport models of dissolution experiments in geothermal reservoirs.

Modeling Approach

The simulations were carried out using the non-isothermal reactive geochemical transport code TOUGHREACT (Xu and Pruess, 2001; Xu et al., 2004a). This code was developed by introducing reactive chemistry into the framework of the existing multi-phase fluid and heat flow code

TOUGH2-V2 (Pruess et al., 1999). More information on TOUGHREACT can be found at the website <http://www-esd.lbl.gov/TOUGHREACT/>.

Interactions between mineral assemblages and fluids can occur under local equilibrium or kinetic rates. The gas phase can be chemically reactive. Precipitation and dissolution reactions can change formation porosity and permeability, and can also modify the unsaturated flow properties of the rock. The simulator can be applied to 1-, 2-, and 3-dimensional porous, fractured media with physical and chemical heterogeneity. It can resolve multi-component behavior for species present either in liquid, solid, or gaseous phases.

Fluid and Heat Flow Conditions

A simplified two-dimensional grid representing the flow reactor is shown in Figure 5. The flow reactor is modeled using five layers: 4 sublayers consisting of the Texas limestone, and an empty layer simulating the flow around the outside of the reactor. All layers are 30 increments long totaling the actual length of the rod of approximately 0.15 m. The total volume (approximately $7.36E-5 \text{ m}^3$) of the limestone rod is preserved. The limestone layers have the hydrologic and thermal properties as shown in Table 1. The layer representing empty space

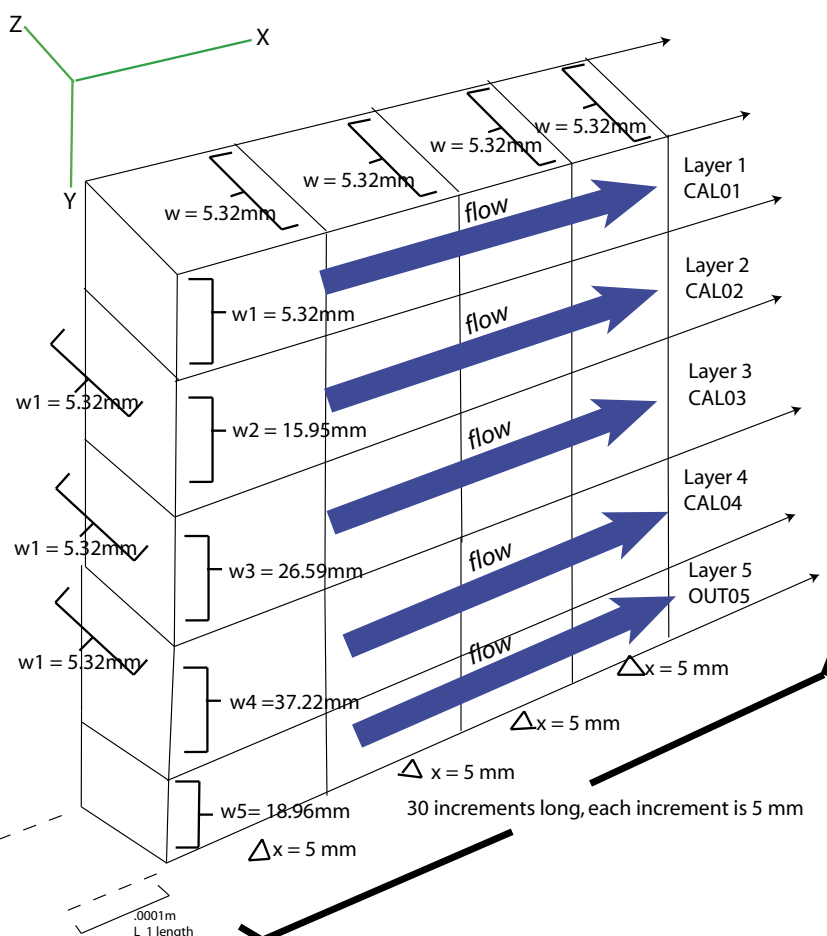


Figure 5. The geometric model of the laboratory flow reactor.

is assigned contrastingly high porosity, permeability, and tortuosity values. Reaction conditions for the case of de-ionized water were input into the model. Results of these initial model runs will be used to calibrate the model.

Table 1. Hydrologic and thermal parameters assigned to the limestone.

Parameters	Limestone
Density (g/m ³)	2710
Permeability (m ²)	1.0E-9
Porosity	0.20
Thermal Conductivity (W* m ⁻¹ K ⁻¹)	3.0
Tortuosity	0.3

Simulation Setup

Our conceptual model considers five one-dimensional flow tubes between the injection and output points, simulating flow through each of the sublayers of the reactor rod. The numerical experiments were conducted under isothermal conditions (21°C-204°C) and at atmospheric pressure. As in the bench top experiments, a constant injection rate was specified, with the flow rate set at 0.5mL/min. The simulations were run for a total time of 1.5 days. Changes in fluid pH, porosity, permeability, fluid temperature, and changes in mineral abundance were monitored over the entire length of the rod over time. Mineral abundance changes were reported in terms of moles of calcite dissolved as a function of distance along the sample cylinder. Changes in porosity were calculated as a function of mineral dissolution and/or precipitation. Porosity increases indicated that mineral dissolution is dominant for these experiments. Changes in permeability were calculated from changes in porosity as described above.

Initial Results

Shown in Figures 6 and 7 below are preliminary results of the numerical experiments simulating the laboratory bench top dissolution experiments. At a constant temperature of 22°C, simulations were run varying pH from 2 to 12 at injection rate of 0.5 mL/min. The graph displaying calcite dissolution versus distance as a function of pH for Layer 4 (the outermost layer of the limestone rod) is shown in Figure 6. From this graph, it is evident that the amount of calcite dissolution varies inversely with pH, as expected. Also, dissolution occurs to a greater degree in the nearer the injection end of the reactor. This effect is especially strong at low pH. The anomalously high dissolution at the exit of the reactor is unexplained and may be the result of a numerical artifact.

Another set of simulations was run keeping pH constant at 4 while varying the injection rate from 0.05 mL/min to 50 mL/min. A graph displaying calcite dissolution versus distance as a function of varying injection rate for Layer 4 is shown in Figure 7. From this graph, it is evident that the amount of calcite dissolution varies directly with the flow rate, as would be expected. Also, dissolution occurs to a greater degree in the near vicinity of the injection point. This effect gets stronger

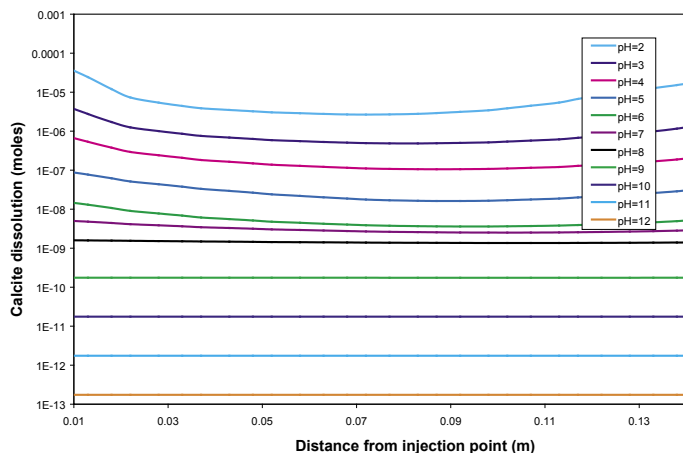


Figure 6. Calcite dissolution versus distance from the injection point at time = 1.5 days after injection begins while varying pH.

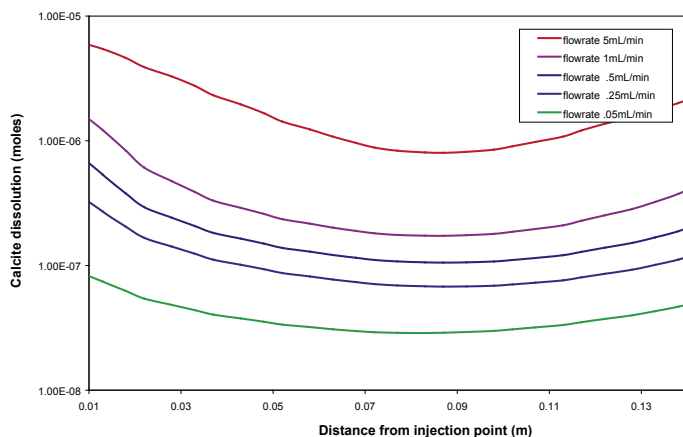


Figure 7. Calcite dissolution versus distance from the injection point at time = 1.5 days after injection begins while varying the injection rate.

with increased flow rate. Again, the anomalously high dissolution at the exit of the reactor is unexplained and may be the result of a numerical artifact.

Summary and Conclusions

Two chelating agents, EDTA and NTA, were investigated for use as mineral-dissolution agents in geothermal wellbores and in near-wellbore formations. A laboratory reactor was designed and fabricated for simulating the dissolution of calcium carbonate (Texas Limestone) using these and other dissolution agents under controlled conditions that simulate a geothermal reservoir. Preliminary experimental data indicate that both EDTA and NTA are effective dissolution agents and that dissolution capacity increases with temperature. A reactive transport model of the laboratory reactor was constructed using TOUGHREACT for the purpose of simulating the calcite-dissolution process. Initial results indicate that, as expected, dissolution rate is directly proportional to flow rate, but indirectly proportional to pH. Further laboratory experiments will proceed with the objective of optimizing ex-

perimental conditions and of extending the range of reactants. Further modeling work will be conducted with the objective of simulating the calcite-dissolution process in the presence of chelating agents, acids, and bases.

Acknowledgements

This work was supported by the Department of Energy under grant DE-FG36-04GO14295 which does not constitute an endorsement of this paper.

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