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THE *IN SITU* FORMATION OF CALCIUM CARBONATE AS A DIVERSION AGENT FOR USE IN ENGINEERED GEOTHERMAL SYSTEMS

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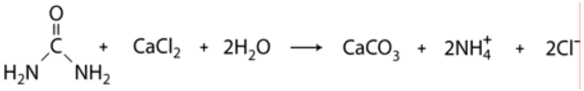
ABSTRACT

In the creation of Engineered Geothermal Systems, water is typically injected at pressures just below the least principal stress of the formation in order to open, through shear failure, partially sealed fractures that intersect the wellbore. Once a fracture (or set of fractures) is created, however, the stimulation fluid flows into the newly created fractures and is unavailable for subsequent fracture stimulation elsewhere along the wellbore. Fluid diversion agents are compounds that can serve to temporarily plug newly stimulated fractures and make the injected water available to stimulate new fractures. The diversion agent is subsequently removed to allow for flow from those previously sealed fractures. The in situ precipitation of calcium carbonate was studied for use as a diversion agent in Engineered Geothermal Systems. Urea thermally decomposes starting at about 150°C to ammonium and carbonate. In the presence of $CaCl_2$ the carbonate subsequently precipitates to form $CaCO_3$. This series of reactions was studied using a high temperature/pressure flow reactor over the range of 140-190°C. Results indicate $CaCO_3$ formation increases nonlinearly as a function of temperature.

EXPERIMENTAL APPROACH

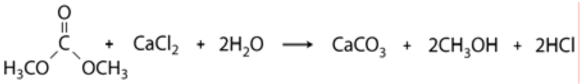
Chemical Reactions

The reaction to form the in situ precipitation of $CaCO_3$ involves the first order decomposition of urea to create carbonate in the presence of $CaCl_2$:



$$H_2N{-}C(=O){-}NH_2 + CaCl_2 + 2H_2O \longrightarrow CaCO_3 + 2NH_4^+ + 2Cl^-$$

Urea decomposes readily at and above 150°C to form carbonate, which subsequently reacts immediately with Ca to form calcite. Similarly, dimethyl carbonate decomposes at high temperature in the presence of calcium chloride to form calcite:



$$H_3CO{-}C(=O){-}OCH_3 + CaCl_2 + 2H_2O \longrightarrow CaCO_3 + 2CH_3OH + 2HCl$$

Either reaction can serve to create a supersaturated solution of the naturally occurring mineral calcium carbonate, which serves to occlude fractures and redirect flow.

Reaction under Flowing Conditions

The schematic below shows the high-temperature flow reactor used in these experiments (Figure 1). The design of this reactor was previously described (Mella et al., 2006).

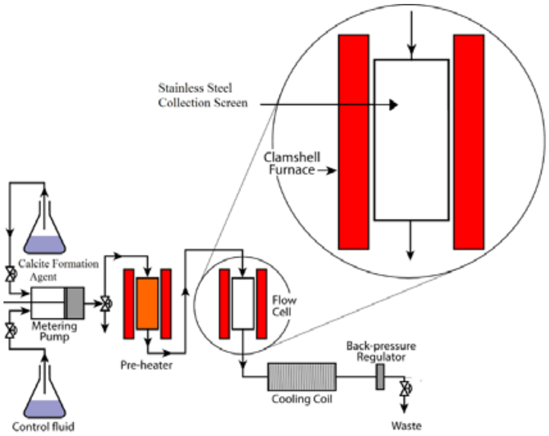


Figure 1. Schematic drawing of the high-temperature flow reactor.

In the first experiment, a Waters HPLC pump was used to keep a constant flow rate of 2.0 ml/min throughout each reaction. A solution of 0.1M urea and 0.1M $CaCl_2$ was flowed through the reactor.

Once the flow stabilized, the chamber was brought to temperature using a two-point-thermocouple heating-control approach. A back pressure regulator was used to maintain sufficient pressure to ensure that the solution in the reactor did not boil. To favor formation of $CaCO_3$, the solution pH was adjusted to pH 11, which is slightly above the pK_a of bicarbonate. After a reaction time of approximately 3 hours, the heater was turned off and deionized water was flushed through the system.

The photographs below show the flow cell and its $CaCO_3$ deposits following a reaction at 190°C.

Figure 2. $CaCO_3$ crystals formed within the flow cell during an experiment at 190°C.

Figure 3. $CaCO_3$ crystals that formed at the bottom of the reactor on a metal screen at 190°C.

The $CaCO_3$ that precipitated during the experiment was removed from the reactor and weighed. The molar yield was then calculated based the amount of calcium pumped through the reactor over the course of the experiment. The molar yield was calculated by dividing the moles of calcium recovered by the total moles of calcium that flowed through the reactor. These data are graphed in figure 4 below:

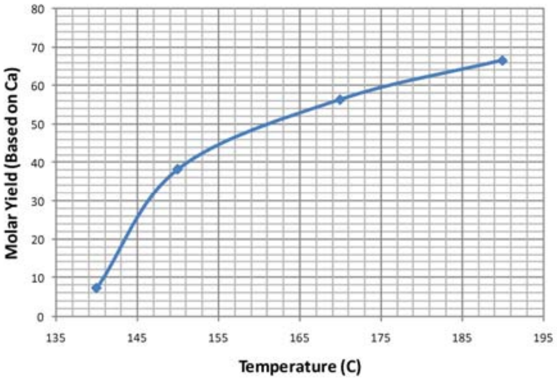


Figure 4. $CaCO_3$ precipitated as a function of temperature within the flow reactor upon the thermal decomposition of urea.

In a second set of experiments, the metal-mesh screen that had been placed within the reactor flow cell was removed and the flow cell was filled with particles of calcium carbonate. This was intended to simulate the effect of the presence of sized calcium carbonate within the reagent solution. A solution containing 0.5M each of urea and $CaCl_2$ was pumped through the flow cell at 2 mL/min. The temperature within the flow reactor was maintained at 150°C. In spite of the fact that the reaction time was reduced to 1 hour and 45 minutes and the temperature was reduced by 40^oC, significantly more $CaCO_3$ was formed (see Figures 5 and 6). This was due in part to the presence of the sized calcium carbonate that provided innumerable nucleation sites within the reactor, but also to the fact that the concentrations of urea and $CaCl_2$ were both 5 times greater than in the first experiment. Photos of the reactor after the experiment are shown in figures 5 and 6 below:

Figure 5. Side view showing the formation of calcium carbonate at the entrance of the flow cell

Figure 6. Top view showing the formation of calcium carbonate at the entrance of the flow cell

The reactor was reassembled and the experiment was resumed, resulting in the plugging of the flow cell. As the flow cell plugged, the pressure in the pump reached a pre-set limit of 1800 psi and the pump shut itself off. Figure 7 below shows the pressure vs. time plot.

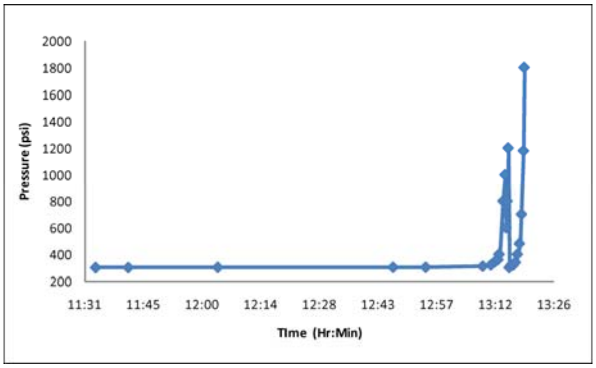


Figure 7. Pressure inside the reactor as a function of time in an experiment wherein the reaction was allowed to proceed until the reactor plugged. The flow cell had been previously filled with sized calcium carbonate particles.

Figure 8 shows an expanded view of Figure 7 that magnifies the portion of the curve at which time the reactor was plugging.

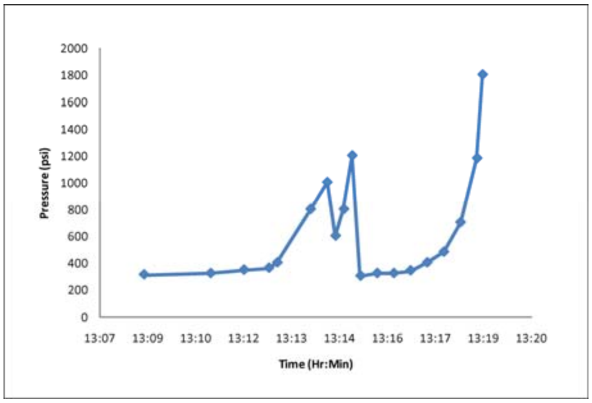


Figure 8. Expanded view of the pressure vs. time plot of the previous figure. The early spikes in pressure show preliminary bridging followed by collapse before the flow cell finally and permanently sealed itself.

Reaction under Batch Conditions

In the experiments listed in Table 2, urea, $CaCl_2$, and various proprietary (Halliburton) viscosifiers such as Thermavis and Thermacheck were mixed according to proscribed proportions and heated to $204^{o}C$ in a 500-cc batch autoclave reactor. In each instance, the heated solution was then held at that temperature for a duration of 4 hours. The objective was to determine if urea could be made to decompose and form $CaCO_3$ as observed in the flow reactor.

Table 2. Conditions for Thermal Decomposition of Urea in Batch Autoclave Reactor

#	*Experimental Conditions*	*Comments*
1	0.5M urea and 0.5M $CaCl_2$	204°C for 4 hours. Brown-colored solid produced in a dark watery solution.
2	10 M urea, 10 M $CaCl_2$, 20 M $CaCO_3$	204°C for 4 hours. Crumbly brown solid produced smelling of NH_3. Calcite cemented to liner.
3	10 M urea, 10 M $CaCl_2$, 20 M $CaCO_3$, 2.85 g Thermavis, 2.85 g Thermacheck	204°C for 4 hours. Products consisted of a crumbly brown solid smelling of NH_3.

In the first experiment, 0.5 M urea and 0.5 M $CaCl_2$ were mixed in equal proportions and heated to $204^{o}C$ for 4 hours. After cooling, the autoclave was opened to reveal a brown, amorphous solid in a dark watery solution (see Figure 9).

In a second experiment, 20 M sized calcium carbonate was placed in the reactor and the experiment was again conducted with urea and $CaCl_2$, but with the concentrations of each increased to 10 M. The reaction product was a brown, crumbly solid plus some calcite cemented to the liner.

Figure 9. Photograph of the reaction products from Experiment 1 in Table 2.

In the third experiment, proprietary Halliburton viscosifiers Thermavis and Thermacheck were added to the previous mixture in proscribed proportions. Shown in figure 10 below are the contents of the reactor after experiment 3. It is evident that, as in previous experiments, no pure $CaCO_3$ precipitate formed. Rather, the reaction product was a dark crumbly substance.

Figure 10. Photograph of the reaction products from Experiment 3 in Table 2.

It is possible that since ammonia (or ammonium ion) is a break-down product of urea, it interferes with the formation of calcite in the batch reactor. In contrast, in the flow reactor, ammonium ions are flushed away from the precipitating calcite—thereby not interfering with the formation of calcite.

The observation of such contrasting product compositions, depending on whether urea is made to decompose in a flow reactor or in a batch reactor, has implications for its use as a flow diversion agent in geothermal wellbores. As the solution of urea/$CaCl_2$ is pumped down a wellbore and into permeable fractures, $CaCO_3$ should form, as observed in the flow reactor, so long as there is continuous flow of the solution into the fractures. As soon as the solution stagnates, however, it appears that a pure $CaCO_3$ no longer crystallizes out of solution. Instead, a brown, crumbly “precipitate” forms. It has the consistency of sandy soil and may still plug fractures and serve as an adequate fluid-diversion agent, but it does not possess the structure integrity of the $CaCO_3$ that was formed and observed in the flow experiments.

SUMMARY AND FURTHER WORK

The *in situ* precipitation of calcium carbonate through the thermal degradation of urea in the presence of $CaCl_2$ was studied for use as a diversion agent in Engineered Geothermal Systems. Results indicate that $CaCO_3$ starts to deposit at about 150^{o}C and that the rate increases nonlinearly as a function of temperature at least as high as 190°C. Further investigations will include the thermal degradation of methyl carbonate as well as the use of catalysts to lower the temperature and/or increase the rate of the thermal decomposition of urea and/or methyl carbonate.

REFERENCES

Mella, M., Rose, P.E., Kovac, K., Xu, T., Pruess, K., and McCullough, J., (2006) Calcite Dissolution in Geothermal Reservoirs Using Chelants: *GRC Transactions,* San Diego, California.