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The Testing of Fluorescein Derivatives as Candidate Geothermal Tracers

Y.L. Wong and P.E. Rose

Energy and Geoscience Institute, University of Utah,
423 Wakara Way, Suite 300, Salt Lake City, UT 84108

ABSTRACT

Eight fluorescein derivatives were tested for use as geothermal tracers. Four of these candidates were observed to be significantly more detectable than the other four and were subsequently tested for thermal stability. They were subjected to conditions that simulate a hydrothermal environment in laboratory reactors at a temperature of 270°C for 48 hours. They were then analyzed by High Performance Liquid Chromatography (HPLC) to determine how much they had thermally decomposed by comparing the concentrations of the reacted samples to that of the controls. These initial screening tests have revealed that two of the tracers, fluorescein-5-(6)-sulfonic acid and 5-(6)-carboxyfluorescein, possess comparable thermal stability to fluorescein. It was discovered that 5-carboxy-2',7'-dichlorofluorescein decomposed upon heating to give 5-carboxyfluorescein.

Introduction

With the increase in demand for more thermally stable and detectable tracers in geothermal industry, the search for more new candidates has become an important task. One of the most important properties required of geothermal tracer is a low detection limit (Adams and Davis, 1991). A geothermal tracer with a low detection limit can greatly reduce the amount of tracer used in tracer injection tests, thus reducing cost. Another requirement is thermal stability. A geothermal tracer must possess sufficient thermal stability to passage through the reservoir with either no thermal decay or a slow but well characterized rate of decay. Until recently, fluorescein was the only geothermal tracer that possessed both low detection limit and good thermal stability.

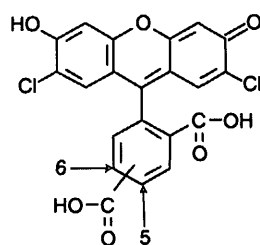
In this study, eight fluorescein-derivative tracer candidates were tested for their detectability and thermal stability: 5-(6)-carboxy-2',7'-dichlorofluorescein (compound A), fluorescein-5-(6)-sulfonic acid (compound B), 5-(6)-carboxy-4',5'-dimethylfluorescein (compound C), 5-(6)-carboxyfluorescein (compound D), Oregon Green 488 (compound E), 6-carboxy-4',5'-dichloro-2',7'-dimethoxyfluorescein (compound F), Oregon

Green 514 carboxylic acid (compound G) and Oregon Green 500 carboxylic acid (compound H). Based on the results of the detectability test, four of these candidates were chosen for the thermal stability screening test, in which they were subjected to simulated hydrothermal conditions (270°C, 48 hours) in laboratory experiments. Two of them, compounds B and D, were proven to be thermally stable with an average residual concentration of at least 50%. These two compounds were further tested at 280°C and 290°C for the same duration.

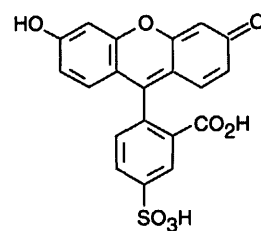
Experimental Procedure

For the detection limit test, 1 mg of each candidate (see Figure 1, overleaf) for structural formulas) was dissolved into 1000 ml of deionized water. The 1-ppm solution was further diluted by 1000 ml of deionized water to form a 1-ppb aqueous solution. The tracer candidate solutions were then analyzed by HPLC with fluorescence detection (Water Corporation, Milford, MA). The column used was a silica-based C-18 (Keystone Scientific, Inc. BetaBasic-18 150 mm x 3 mm) and was kept at 30°C at all times. The excitation and emission wavelengths of the fluorescence detector were 488 nm and 514 nm, respectively. The mobile phase consisted of 40% methanol, 5 mM tetrabutyl ammonium phosphate (TBAP), and 4.71 mM phosphate buffer. The flow rate was 0.65 ml/min. The injection volume was 10 µl. Based on the strength of the signal response, the concentration of the tracer-candidate solution was adjusted so as to achieve a signal-to-noise ratio of three to one. Four out of eight tracer candidates, A, B, D and H, had detection limits lower than 10 ppt were chosen to continue onto the thermal stability test.

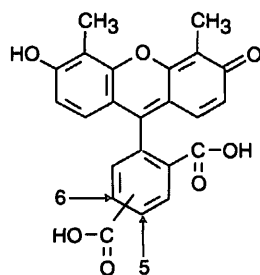
In order to test the four chosen tracer candidates for their resistance to thermal degradation, each was exposed to a simulated geothermal environment at a target temperature for a given period of time. The four tracer candidates were diluted with simulated geothermal reservoir fluid from a concentration of 1 ppm to 25 ppb. The pH was adjusted to 6.5 at room temperature. 30-ml quartz ampules were used to hold about 18-ml of



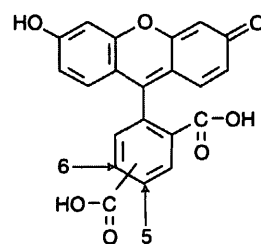
Cpd. A: 5(6)-carboxy-2',7'-dichloro-fluorescein



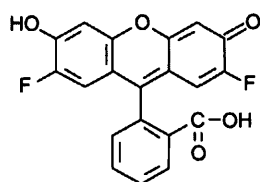
Cpd. B: fluorescein-5-sulfonic acid



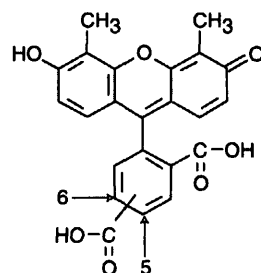
Cpd. C: 5(6)-carboxy-4',5'-dimethylfluorescein



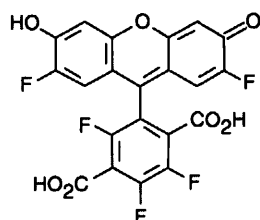
Cpd. D: 5(6)-carboxyfluorescein



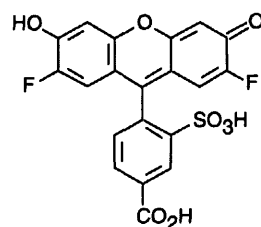
Cpd. E: 2',7'-difluorofluorescein



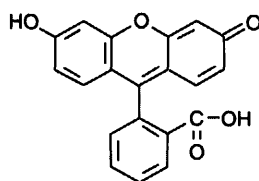
Cpd. F: 6-carboxy-4',5'-dichloro-2',7'-dimethylfluorescein



Cpd. G: Oregon Green 514



Cpd. H: Oregon Green 500 carboxylic acid



fluorescein

Figure 1. Structural formulas of the candidate fluorescein derivatives.

the tracer candidate solution. The solution inside the ampules was purged with argon to remove oxygen. They were then sealed using an oxy methane flame. During sealing, the neck of the ampule was aspirated to prevent oxygen contamination from the oxy methane flame. For each tracer candidate, four ampule-solutions were made, three of them serving as samples and one serving as the control. The three sample ampules were put into a water-filled, one-liter stationary autoclave (Autoclave Engineers, Philadelphia, PA). The autoclave was then heated to the target temperature. About 2 to 2.5 hours was required to reach the desired operational temperature. The ampules were left inside the autoclave at the desired temperature for 48 hours. The pressure inside the autoclave was the pressure of steam under saturated conditions at the target temperature. The cool-down time was about 4 hours.

After the autoclave cooled, the ampules were removed and unsealed. The sample and control solutions were diluted from 25 ppb to 250 ppt. Since there might have been small pieces of glass present in the samples and control during the process of unsealing the ampules, the samples were filtered using 0.45 μm filter paper and subsequently analyzed by HPLC.

Results and Discussion

Table 1 compares the detection limit of the eight tracer candidates in both molarity and ppt by weight.

Table 1. Detection limits for eight tracer candidates.

| Compound | Detection Limit (M) | Detection Limit (ppt) |
|-------------|------------------------|-----------------------|
| A | 2.25×10^{-11} | 10 |
| B | 2.09×10^{-11} | 10 |
| C | 2.47×10^{-10} | 100 |
| D | 2.66×10^{-11} | 10 |
| E | 2.72×10^{-10} | 100 |
| F | 1.98×10^{-8} | 10,000 |
| G | 1.95×10^{-10} | 100 |
| H | 4.46×10^{-12} | 2 |
| Fluorescein | 6.02×10^{-12} | 2 |

Table 2 compares the average residual concentration and the retention times, the times elapsed between the injection point and the peak maximum (Scott, 1994), of the four most stable compounds. Compounds A and H showed a lower residual concentration relative to compounds B and D, indicating that compounds A and H were less thermally stable.

Table 2. Undecayed percentages and retention times for fluorescein and four fluorescein derivatives.

| Compound | Undecayed Percentage (%) | Retention Time* (min) |
|-------------|-----------------------------------|-----------------------|
| A | 6.88 ± 1.78 | 7.47 |
| B** | 61.6 ± 7.63 , 56.0 ± 7.47 | 5.23, 8.08 |
| D** | 85.5 ± 5.36 , 78.0 ± 3.74 | 4.64, 7.45 |
| H | 30.1 ± 4.79 | 9.61 |
| Fluorescein | 77.9 ± 3.20 | 22.2 |

* Based on 40% methanol buffer solution with 5 mM TBAP.

** There are two separate peaks for the two isomers in compounds B and D.

Figure 2 shows the chromatogram for the reacted compounds A and D. We discovered that compound A thermally degraded to give a product that has the exact same retention time as one of the isomers of compound D (Peak 1 of compound D). This suggested that compound A decomposed to give one of the isomers of compound D. Upon injection of one of the pure isomers

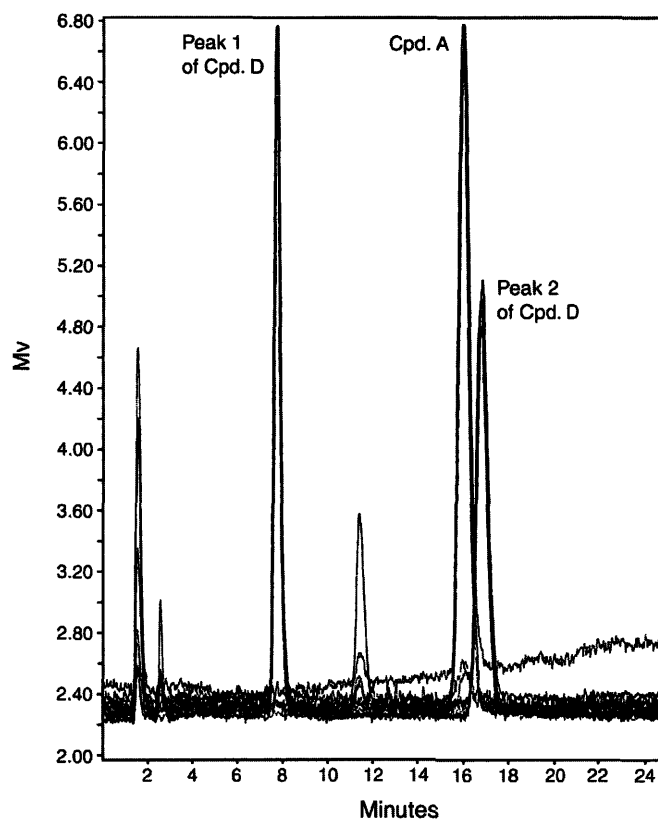


Figure 2. Chromatogram of compounds A and D.

of compound D (5-carboxyfluorescein), it was discovered that 5-carboxyfluorescein has the same retention time as peak 2 of compound D. Thus, we reached the conclusion that peak 2 of compound D was 5-carboxyfluorescein. Therefore, the product produced by thermally decomposing compound A was 6-carboxyfluorescein (peak 1 of compound D). Thus, it was suspected that the original compound A was mostly 6-carboxy-2',7'-dichlorofluorescein (peak 3). Since there was just one dominant peak in the chromatogram of compound A, the other isomer (5-carboxy-2',7'-dichlorofluorescein) was missing. Notice that there was also a small peak at about 11.4 minutes. Upon injecting the thermally tested sample of compound A, it was noticed that the small peak at 11.4 minutes increased in amplitude. We suspected the peak was 6-carboxymonochlorofluorescein with a chlorine atom attached at either the 2' or 7' position (compound A, Figure 1). This could be an intermediate in the thermal degradation of compound A.

Since compounds B and D demonstrated good thermal stability at 270°C and 48 hours, they were further tested at 280°C and 290°C for the same duration. Table 3 compares the undecayed percentage for the different temperatures. As expected, the undecayed percentage decreased as the experimental temperature increased.

Table 3. Undecayed percentage of compounds B and D at different temperatures and 48 hours.

| Temp Compd / | Undecayed Percentage at 270°C (%) | Undecayed Percentage C at 280° (%) | Undecayed Percentage at 290°C (%) |
|-----------------|--|---|--|
| B Peak 1 | 61.6 ± 7.63, | 37.0 ± 0.356, | 21.9 ± 0.655, |
| B Peak 2 | 56.0 ± 7.47 | 28.4 ± 0.946 | 14.4 ± 0.419 |
| D Peak 1 | 85.5 ± 5.36, | 61.5 ± 3.88, | 39.0 ± 1.85, |
| D Peak 2 | 78.0 ± 3.74 | 49.7 ± 3.65 | 25.9 ± 1.00 |

At all three temperatures, the first peak of compound D has a higher undecayed percentage than the second peak in the thermal stability test, indicating that 6-carboxyfluorescein has better thermal stability than 5-carboxyfluorescein. Similar to compound D, the first peak of compound B also has a higher undecayed percentage than the second peak.

From the thermal stability tests, there is a trend that compounds that do not have halogen groups (compounds B and D, Figure 1) attached to any position of the compound, tend to have higher thermal stability in comparison to halogenated compounds. Hence, halogen groups may be responsible in part for the thermal degradation of the compound upon heating in the autoclave. In fact, we observed the thermal degradation of compound A into its non-halogenated counterpart, compound D. We also suspect that compound H thermally degraded into a non-halogenated product(s) that does not fluoresce.

Conclusions

In this study, we demonstrated the detectability of eight fluorescein derivatives in an attempt to find suitable new tracers for the geothermal industry. Four out of those eight compounds, namely, 5-(6)-2',7'-dichlorofluorescein, fluorescein-5-(6)-sulfonic acid, 5-(6)-carboxyfluorescein and Oregon Green 500 carboxylic acid were picked to undergo the thermal stability test. We identified two out of four compounds that possess comparable thermal stability to fluorescein. Those two compounds are fluorescein-5-(6)-sulfonic acid, and 5-(6)-carboxyfluorescein. We intend to further test the other two compounds, 5-(6)-2',7'-dichlorofluorescein & Oregon Green 500 carboxylic acid, at lower temperatures to fully explore their use as geothermal tracers in lower-temperature systems. We also discovered that fluorescein derivatives that contain halogen groups are likely to be less thermally stable than their unhalogenated counterparts. We discovered that 5-(6)-2',7'-dichlorofluorescein degraded into 6-carboxyfluorescein.

Acknowledgments

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References

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