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FIBER OPTIC BASED PH MEASUREMENT IN A GEOTHERMAL BRINE

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ABSTRACT

The measurement of pH is well established. Since pH can affect reaction rates, system corrosion, and water quality, on-line electrodes have been commercialized. These devices necessarily contain a porous membrane to allow the flow of hydrogen ions to provide electrical potential for measurement. In a recent application to a geothermal solution, electrode fouling was experienced, even with considerable sample conditioning. As an alternative, we designed and constructed an in-line pH instrument based on the spectroscopic absorption of acid-base indicator dyes. The instrument introduced bromocresol green into the stream via a static mixer and measured the ratio of the characteristic acidic and basic absorption bands using an in-line fiber optic cell. Details of the design and its application will be presented.

2. INTRODUCTION

Geothermal power promises to be an environmentally clean and efficient method of generating electricity. Simply, this process utilizes the steam evolved by hot brine (>200°C, see Figure 1), pumped from wells located several thousand feet below the earth's surface, to turn electrical turbines. Red Hill Geothermal, Inc. has built four plants in southern California's Imperial Valley desert. Although all the plants are operating successfully, the plethora of elements contained in the brine continues to challenge chemists and engineers. pH is of particular interest since it effects the extent of corrosion. On-line pH electrodes fail due to the high concentration of dissolved solids, particularly silica, which plug the glass membrane and render the electrodes inoperative. The accuracy of laboratory pH determinations for grab samples was uncertain due to temperature changes and/or air oxidation of metal ions present

(eg. Fe(II) → Fe(III), liberating hydrogen ions).

Recently, fiber optic chemical sensors have been designed to measure blood chemistry, including pH.¹ These sensors incorporate a pH sensitive dye in a polymeric substrate located on the tip of an optical fiber. Drawing on this concept, we have designed a pH sensor which mixes a dye indicator with the sample and measures the absorbance at a flow-through cell interfaced to a visible spectrometer via fiber optic cables. This report covers instrument design, laboratory calibration and initial in-line data.

3. EXPERIMENTAL

The instrument (see Figure 2, Table 1) was designed to introduce aqueous bromocresol green into the stream via a static mixer and to measure the absorbance of the characteristic acidic (450 nm), basic (616 nm) and isosbestic (510 nm) bands at an in-line fiber optic cell. The system was calibrated, pH vs. absorbance, by preparing 16 samples of 0.05 mM dye in citrate or phosphate buffer. For each sample, 10 spectra were averaged at 2 nm resolution on a Guided Wave model 200 spectrometer. Peak heights were obtained using the "peak" subroutine (see Figure 3, Table 2). A plot of the peak heights at 450 and 616 nm in Figure 4 shows the expected pH dependence and optimum measurement range of 3.5 to 5.5. This data was then used to determine the extinction coefficients, ϵ_A^λ and ϵ_B^λ at 450 and 616 nm and at a pH of 2.14 and 6.21 for the acid and base forms of bromocresol green;²

$$\epsilon_{2.14}^{450} = \left(\frac{[H^+] + K_a}{[H^+]} \right) \frac{A}{C} = 1.511 \times 10^4 M^{-1} cm^{-1} \quad (1)$$

and

$$\epsilon_{6.21}^{450} = \left(\frac{[H^+] + K_a}{[K^a]} \right) \frac{A}{C} = 1.903 \times 10^3 M^{-1} cm^{-1} \quad (2)$$

similarly

$$\epsilon_{2.14}^{616} = 1.012 \times 10^3 M^{-1} cm^{-1} \quad (3)$$

$$\epsilon_{6.21}^{616} = 3.833 \times 10^4 M^{-1} cm^{-1} \quad (4)$$

where A is the measured absorbance, K_a the dye acid equilibrium constant, which ranges from 1.656×10^{-5} to 2.5×10^{-5} for an ionic strength of 0.02 to 0.5 M (the former is used in the calculations above), and C is the dye concentration (determined at the isosbestic wavelength with ϵ_{510}^{ISO} , calculated as $5.3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$). These values were used in the following equations derived by introducing the acid equilibrium constant into Beer's Law:²

$$A = \frac{\epsilon_A^\lambda [H^+] + \epsilon_B^\lambda K_a}{[H^+] + K_a} C \quad (5)$$

or

$$[H^+] = K_a \left(\frac{\epsilon_B^\lambda - \frac{A}{C}}{\frac{A}{C} - \epsilon_A^\lambda} \right) \quad (6)$$

and

$$pH = -\log[H^+] \quad (7)$$

to generate a pH vs. absorbance curve to fit the standard data (see Figure 4). Since the K_a is dependent on ionic strength, the two values quoted above were used to bracket the standards. In addition, a straight line fit based on the Henderson-Hasselbach equation was determined by fitting the data to a log plot (see Figure 5) resulting in the following concentration independent equation:³

$$pH = 1.068 \log\left(\frac{A616}{A450}\right) + 4.309 \quad (8)$$

Since the acid equilibrium constant varies according to:

$$K_a = e^{-\Delta G/RT} \quad (9)$$

its temperature dependence can be calculated. Specifically for the on-line value of 85°C (358°K):

$$\ln K_a^{358} = \left(\frac{297}{358}\right) \ln K_a^{297} \quad (10)$$

which yields K_a^{358} equal 3.97, corresponding to a 0.8 pH shift. Measurement of the absorbance spectra of bromocresol green over this temperature range at a pH of 4.4 shows a decrease in absorbances at both wavelengths (see Figure 6), but only

corresponds to a 0.05 pH reduction at 85°C using equation (8). There is insufficient data to rigorously predict the pH temperature dependence from equations (6) and (7). However, if we assume the decrease in absorption at the isosbestic wavelength represents a decrease in dye concentration (due to decomposition, volatilization, etc.), and we substitute this concentration into these equations, we obtain a decrease in pH of 0.09 at 450 nm and 0.04 at 616 nm. Or if we assume the concentration is constant and the decrease in absorption represents a decrease in absorptivity, we obtain identical results.

4. RESULTS AND DISCUSSION

Although it is desirable to know the pH throughout this geothermal process, the instrument was installed near the exit section of the plant, just prior to re-injection of spent brine into the ground. This location was chosen since it exhibits minimal suspended solids and moderate temperature and pressure (85°C and 8 psig). The instrument collected data for several hours over a two day period. The spectra were then analyzed to determine pH using the equations (6), (7) and (8) (see Figure 7). The dye was changed after the first hour producing tilt in the subtracted background. The effect was most pronounced at low wavelengths, resulting in low pH values calculated from the 450 nm data. Subtraction of a new background corrected this offset and yielded good correlation between methods. The average pH for this period based on equations (6) and (7) is 5.28 at 450 nm and 5.04 at 616 nm, respectively, and 5.16 based on equation (8). Equal weighting of these values yields an average pH and standard deviation of 5.16 ± 0.10 . Several excursions are also evident in Figure 7 and are attributed to the formation of bubbles, which are occasionally observed in the transparent flow meter during data collection (replacement of worn fittings corrected this problem).

5. CONCLUSIONS

A sensor based on the absorbance of bromocresol green successfully measured the pH of Red Hill Geothermal, Magma Power plants exit brine at 5.16 ± 0.10 . This value corroborates pH measurements of anaerobically collected grab samples taken at this location. This study also represents a "first pass" instrument design, which is currently undergoing evaluation. The pH was determined from both a theoretical equation and a simple algorithm, yielding nearly identical results. This algorithm's merit is its independence of dye concentration.

Future work will involve measurements at additional plant locations.

6. REFERENCES

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3. Peterson, J.I., 1988, "Chemical, Biochemical, and Environmental Application of Fibers", SPIE,990, pp. 1-17, or Wolfbeis, O.S., et.al., and Baldini, F., et.al., SPIE,1368, 1990, "Chemical, Biochemical, and Environmental Sensors".

7. NOTICE

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Table 1. Components of visible pH sensor. See Figure 2.

- 1 Swagelok, 3/8" 316 SS tubing (unless otherwise specified)
- 2 Pennwalt tube meter, model NPXG-145, 1/4" 316 SS body, 3" glass tube, for process side, set to 43% flow rate (100% = 25 GPH)
- 3 10" x 12" NEMA box
- 4 Swagelok T, 3/8" (mixing point of sample & dye)
- 5 Chemineer Kenics mixer, model 37-06110, 3/8" x 14" (cut in two 7" pieces), 316 SS tubing
- 6a A coil of Teflon tubing, 1/16" OD, 500 um ID, was used to restrict flow
- 6b A 3" length of 1/4" clear Teflon tubing capped off and filled with air, attached to a Swagelok Tee, was used as a pulse dampener (not shown)
- 7 Custom Sensors & Tech., 8009-.05SSC 1/2" Swagelok cross/fiber optic cell, windows were set at 1 cm path distance
- 8a Fluke model 52 thermometer to measure solution temperature via athermocouple which passed through a septum in a Swagelok Tee
- 8b Orion pH meter and Fischer Scientific glass electrode, 13-641-646, optionally passed through the Swagelok Tee, drilled to 1/2" clearance
- 9 Back pressure ball valve
- 10 Sample outlet, to sump
- 11 Guided Wave 500 um fiber optic cables, 20' to a GW Spectrometer model 200 with Toshiba, T3200 lap top computer for spectral acquisition
- 12 1/8" Teflon tubing, from reservoir to pump to mixing coil
- 13 Reservoir of bromocresol green, Fisher Scientific, 0.5 mM, pH adjusted
- 14 FMI lab pump, model RP-650

Table 2. Absorbance data for bromocresol green standards. See Figures 3 and 4.

pH	Absorbance		
	(450-700) nm	(510-700) nm	(616-700) nm
2.14	0.239	0.084	0.016
2.79	0.229	0.084	0.014
2.90	0.231	0.084	0.014
3.37	0.219	0.079	0.029
3.73	0.213	0.082	0.067
4.10	0.219	0.084	0.121
4.31	0.179	0.082	0.067
4.36	0.167	0.081	0.204
4.50	0.149	0.079	0.242
4.62	0.135	0.080	0.275
5.05	0.082	0.076	0.377
5.16	0.067	0.076	0.432
5.46	0.056	0.078	0.493
5.84	0.033	0.070	0.475
6.21	0.027	0.078	0.555
7.12	0.029	0.075	0.540