

APPLICATION OF SODIUM BENZOATE IN SURFACE WATER FLOW MEASUREMENTS IN MINDANAO GEOTHERMAL PRODUCTION FIELD, PHILIPPINES

Adriano C. Cabel Jr., Gabriel M. Aragon, Rogel G. Trazona
and Medardo C. Magdadaro¹

¹PNOC Energy Development Corporation, Ft. Bonifacio, Metro Manila, Philippines 1201

Keywords: Mindanao, sodium benzoate, UV-Vis, reinjection, brine.

ABSTRACT

The tracer dilution method has gained acceptance in the geothermal industry as a substitute to the conventional James Lip Pressure Method for bore output measurement. The former type of measurement in quantifying the water flow along the two-phase and reinjection lines has been adopted by PNOC-EDC. Sodium benzoate was analyzed using UV-Vis spectrophotometer and results compared to those from a more expensive instrument such as HPLC. Field trials using a fabricated delivery system were conducted and were also compared to the commercially available tracer flow test equipment. Results of the initial tests showed good precision of concentration and water flow data. Water flow data obtained through flow test set-up, which used a metering pump, were also compared and gave maximum acceptable variance of 3.6 %. Variations in water flow with time have been used as an aid in reservoir management.

1 INTRODUCTION

Flow measurement using the tracer dilution method has gained popularity in the geothermal producing fields in lieu of the standard James Lip Pressure Method (JLPM). The use of sodium benzoate (NaBz) for the liquid tracer is presently used at PNOC-EDC. However, the laboratory in Mindanao Geothermal Production Field (MGPF) located in Southern Philippines has no capability of quantifying sodium benzoate in brine due to the absence and high cost of HPLC unit. Thus, other methods for quantifying sodium benzoate using UV-Vis spectrophotometer were explored in order to have immediate water flow measurements. The need for immediate results was due to the first time application of calcite inhibitor system for well APO-1D and in order to optimize the injection of inhibitor in the well. The applicability of this approach was tested at MGPF wells undergoing calcite deposition, and/or with calcite inhibition set-up.

This report presents the results obtained on the different tests conducted in MGPF. This over-all activity was guided by the following objectives:

1. To determine the applicability of NaBz as a tracer using a fabricated pressure vessel for water flow measurements in the 2-phase and reinjection lines.
2. To monitor changes in water flow of calcite forming wells in order to determine the rate of massflow decline.
3. To determine changes in waterflow along two phase and reinjection lines with time as an additional tool in reservoir evaluation and management.

2 LABORATORY ANALYSIS

2.1 Theory of Method

The theory involved in quantification through UV analysis is governed by two absorption laws, the Beer and Lambert's Law which also applies to colorimetric analyses. Below is the widely accepted absorption equation:

$$\text{Log}_{10} (I_T/I_0) = \epsilon l c \quad (1)$$

where:

ϵ - molar absorptivity
 l - path length
 c - molar concentration

Aromatic compounds like benzoate ion or benzoic acid has extensive double bond conjugation, which allows electron to move from lower to a higher energy level caused by the absorption of light in the UV region (excitation). This absorption of light followed the above two absorption laws thus benzoate or benzoic acid can be quantified through the absorption equation. Earlier studies identified that there are two absorption peaks for benzoate ion and benzoic acid these are 224 (primary peak)/268 nm (secondary peak) and 230 (primary peak)/273 nm (secondary peak) respectively. Generally, the primary peak is more intense than the secondary peak and benzoic acid has a higher intensity of absorption than benzoate ion for both peaks (Jaffe and Orchin, 1962). The accepted equipment for the quantification of benzoate ion and benzoic acid is the HPLC because of its high sensitivity (up to parts per billion level) and selectivity. However, for water flow measurements in geothermal industry where the expected breakthrough concentration of the chemical tracer can be adjusted in parts per million (ppm) level by varying the dosing rate and injectate concentration, quantification using portable UV spectrophotometer is highly feasible.

2.2 Recovery test

Using the most sensitive wavelength of 230 nm, brine from the MGPF main reinjection line was used as matrix for NaBz recovery test. High recovery was obtained at concentrations at least twice that of the background (Table 1). The amount added to the brine and the actual amount obtained is plotted in Figure 1. The two sets of values are in unity with each other giving a good correlation coefficient value of 0.999.

2.3 Comparison of HPLC results with UV method

Accuracy of the method was evaluated by comparing results obtained from UV-Vis and HPLC on selected TFT samples. Results showed that a maximum of 1.8 % relative difference was noted for samples analyzed at 230 nm (Table 2). With these results, it can be concluded that the UV-Vis analysis has high agreement with HPLC thus it is possible to use this for quantifying sodium benzoate from the water samples with known background concentration.

3 FIELD TESTING

3.1 Background

With the success in the quantification of sodium benzoate using the UV-Vis spectrophotometer analysis, the application of this tracer was immediately adopted as this would give immediate results of water flow measurements. Sodium benzoate, which is also used by Tracer Flow Test (TFT), is thought to be the logical replacement in lieu of $MgCl_2$ since it is also available at that time.

Field testing with the in-house pressure vessel set-up was done to measure water flows of the production and reinjection wells using NaBz as tracers to assess its practical application. The results of water flow measurements using NaBz were compared to that of $MgCl_2$, since latter tracer for flow measurements has already been accepted as in the case of Leyte Geothermal Project. Results of NaBz analysis are immediately obtained due to on-site analysis thus the prospect of using this as a tracer became very attractive.

3.2 Repeatability test

Plateau or breakthrough in a run

Figures 2 and 3 illustrate examples of a plateau or breakthrough curve during tracer injection. A plateau or breakthrough is the part of the curve where a straight or almost stable line is produced. This indicates that there is an homogenous mixing between the injectate and brine. The examples presented are runs on the production well APO-3D and reinjection well KL-1RD. This observation is also shown in Table 3 using the trial runs of SK-4B and MT-1RD.

The error band produced in running well SK-4B has a maximum of ± 1.1 kg/s. Relative to the of 39.9 kg/s, this variance is small with a 2.8% error on the average. In well MT-1RD, maximum error band of ± 3.0 kg/s also appears small relative to the well's flow of 139.1 kg/s. This variance gives about 2.2% error on the average.

Accuracy test

The accuracy test of the pressure vessel on-site (See set-up at Figure 4) was compared to tracer flow test (TFT) which uses a metering pump and also uses similar liquid tracer NaBz. The results obtained from the pressure vessel were close to TFT result which were conducted on the first week of June (Table 4). The results in APO-3D matched. In SP-4D, there was a

slight change of the well head pressure which probably resulted to the slight difference of a 0.9 kg/s flow rate. Among the data presented, the maximum difference of 3.6% was observed in well MT-2RD. This difference however, is still less than the 5% maximum acceptable deviation.

Test application in well SP-4D

The main application of this tracer was initially for trending purposes to monitor changes in water flows of wells affected by calcite deposition i.e. wells SP-4D and APO-1D. Well APO-1D was recently fitted with a calcite inhibition set-up and was put on-line to the fluid collection and disposal system (FCDS). Since there is a limitation on the frequency of bore output measurements using James Lip Pressure Method (JLPM), this type of monitoring can be an important tool in predicting well performance changes as well as the decline rate of production output due to calcite deposition in the well bore.

Well SP-4D after its completion on February 1994 gave power output of 6.0 MWe when it underwent medium term discharge on July 1994. Due to the formation of calcite deposition in the well bore, it experienced a power decline down to 1.0 MWe on February 1998. The well was still put on-line despite of its output due to operational necessity, however the well experienced several choking episodes.

For the well to recover, it was mechanically worked over on February 1998. It was discharged to the atmosphere for bore output measurement, and showed a recovery of 5.3 MWe on March 1998.

The well was put in-service to the FCDS to complete the 52 MWe gross requirement of the MGPf power plant without any chemical inhibition. Without the inhibition system, it was expected that power decline will recur. In anticipation, on-line measurement was used to monitor its output. In the absence of TFT and scarcity of steam, the NaBz technique was used to monitor the water flow of the well. Any change of the water flow detected is assumed to be an indication of output change due to calcite deposition.

Table 5 presents the water flow trends of well SP-4D. The June data of 56 kg/s of water flow at a WHP of 9.8 kscg were being used as benchmark. Next month monitoring conducted on 29 July gave about 47 kg/s water flow at WHP of 9.1 kscg would indicate a suspected decline in output. Another survey was conducted on 31 July which gave 46 kg/s flow at WHP of 9.1 kscg. To compare the result from the benchmarks, the well was throttled on 03 August to attain a well head pressure of 9.8 kscg. The measured water flow was 43 kg/s, thereby confirming the reduction in the expected flow rate. The well after the discovery was discharged to atmosphere for bore output measurement using the JLPM. Result showed a 3.8 MWe power, and this concludes a decline in output from initially recorded 5.3 MWe power potential on March 1998.

With the success in the initial trial runs on Well APO-1D and SP-4D the application of this tracer was expanded to cover

other production wells suspected of having indications of output declines and also in the measurements of brine flows across the whole FCDS.

Aid in interpretation of well processes

At the start of commercial operation of the first phase of development, intensive monitoring of chemical and physical parameters was conducted to assess the response of the reservoir to commercial operation. These were plotted and interpreted to come up with a viable explanation of the different processes brought about by exploitation.

Initially, all of the wells exhibited excess enthalpy. Further exploitation activities brought about changes in well bore characteristics. Most notable of these changes is the increasing trend in the water flow of the discharge coupled with the decline in enthalpy. These changes were accompanied by increases in mineralization of the brine and a decrease in the gas content. Initial interpretation suggests possible effect of reinjection returns. However, further studies showed that the fluid temperature was not affected thereby raising some doubts as to the origin of the new discharge fluid. Tracer tests using sodium fluorescein and I-131 were conducted using the nearest injector MT-2RD. Test using the former gave inconclusive results while the latter confirmed no rapid reinjection returns to the production sector.

Waterflow surveys using sodium benzoate as a tracer on the wells showed increasing amount of water in the discharge. Result of the surveys was correlated with the interpretation of the chemical discharge. Reinterpretation was then arrived at which suggest that the existing two-phase horizon that was initially contributing to the discharge has ceased.

Waterflow surveys in brine lines and reinjection wells

Brine flow measurement along the main brine line was conducted on a monthly basis. The trend showed increasing water flow with continuous exploitation (Figure 5). This observation is consistent with the observed changes in the chemistry of the production wells which showed increase in mineralization that can only come from the liquid phase as well as the notable drop in the discharge enthalpy.

Waterflow trending along the reinjection lines among the individual injectors was done to monitor the loading of each injector. The information gathered in this exercise was used in the formulation of a reinjection strategy for reservoir management.

The tracer dilution method of flow measurements was used to determine and distribute the loading of each injector in order to minimize the effect of reinjection returns to the production sector. In effect, prioritization of each injector was established.

Flow measurement using the orifice method encountered some technical problems as it gave inconsistent results. Evaluation of the orifice method showed that it is readily affected by silica deposition thereby reducing the diameter of the orifice plate. This is a common phenomenon along the brine line. Another problem encountered was the unstable reading of the pressure drop across the orifice plate as 2-phase flow exists along the line. Using tracer dilution method the problems encountered with the orifice method are eliminated.

4 CONCLUSIONS

- (1) Field testing showed good repeatability of concentrations and water flow data, in terms of the following: a) plateau is produced for a single batch of run which indicates homogeneous mixing between the injectate and the brine; b) same day but at different times; and different days.
- (2) Pressure vessel surveys are comparable to tracer flow test using a metering pump with results giving a maximum acceptable variance of 3.6 %.
- (3) Result of the tracer flow test was used to evaluate the rate of deposition for calcifying wells.
- (4) Brine flow measurements was used as an additional tool in explaining the different processes that occurred in the reservoir as a result of continuous extraction of hot fluids.
- (5) Prioritization of injection well utilization was established using this method of monitoring.

5 RECOMMENDATIONS

Analysis of sodium benzoate with the UV-Vis spectrophotometer is invaluable in readily obtaining immediate waterflow results in production and reinjection lines. The analytical accuracy and precision of the simple UV-Vis spectrophotometric method is comparable to the more sophisticated but expensive HPLC methodology. Thus, in simple or starting laboratories, this technique is highly recommended.

The target tracer concentration in the mixed brine should be twice the background and preferably within the range of working standards (dilution is possible if high concentration is obtained).

Analysis of benzoate should be done using the primary wavelength of 230 nm as it is more sensitive as compared to the secondary wavelength of 274 nm. Its application to flow calculations translates to a more precise value with lesser % deviation.

Water flow surveys using the pressure vessel with NaBz as a tracer is preferred over $MgCl_2$ as it can give repeatable and accurate results and also comparable to TFT measurements. Data from these surveys can be used to monitor and assess massflow rate reductions in wells with suspected calcite deposition. This method could also be used to measure water

flowrates in 2-phase lines, brine lines and reinjection wells for reservoir performance assessment.

ACKNOWLEDGEMENTS

This project is a joint effort of Mindanao Geothermal Project and Leyte Geothermal Project chemistry laboratories. The authors wish to thank the management of PNOC-EDC for the permission in the publication of this paper.

REFERENCES

Adams, M.C., Moore, J.N., Fabry, L.G. and Ahn, J. 1991. Thermal Stabilities of Aromatic Acids as Geothermal Tracers. *Geothermics*. Vol. 21. pp 323-339, 1992.

Adams, M.C., Benoit, W.R., Doughty, C., Bodvarsson, G.S. and Moore, J.N. The Dixie Valley, Nevada Tracer Test. *Geothermal Resources Council, Transactions* Vol. 13 October 1989.

Adams, M.C., Buck, C., Copp, J., Hirtz, P. and Lovekin, J. Enthalpy and Mass Flowrate Measurements for Two-Phase Geothermal Production by Tracer Dilution Techniques. *Eighteenth Workshop on Geothermal Reservoir Engineering*, Stanford University, Stanford, California, January 26-28, 1993.

Lovekin, J. and Hirtz, P. Tracer Dilution Measurements for Two-Phase Geothermal Production: Comparative Testing and Operating Experience. *Proceedings of the World Geothermal Congress*, 1995, Florence, Italy.

Lindsay, S. 1992. *High Performance Liquid Chromatography*. 2nd edition.

Jaffe, H.H. and M. Orchin. 1962. *Theory and Applications of Ultraviolet Spectroscopy*. Wiley, New York.

UV-Vis Instruction Manual. Model UV-1601, Shimadzu Corporation.

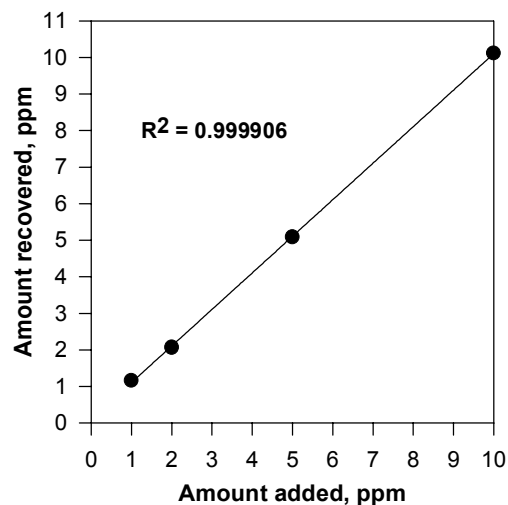


Figure 1. Recovered NaBz in brine matrix versus amount added

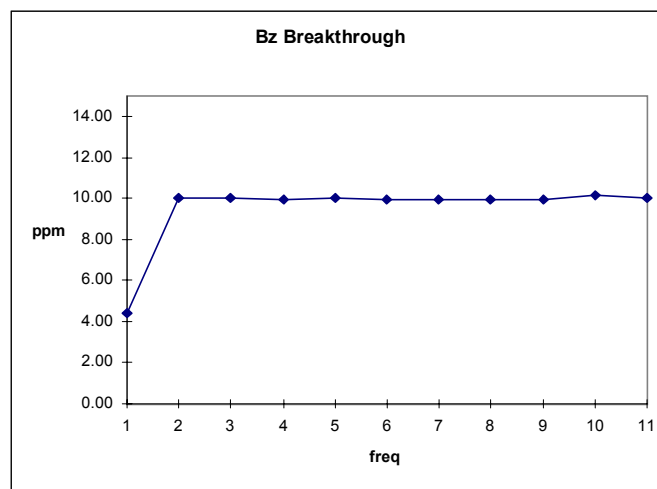


Figure 2. Breakthrough curve in a run in well APO-3D

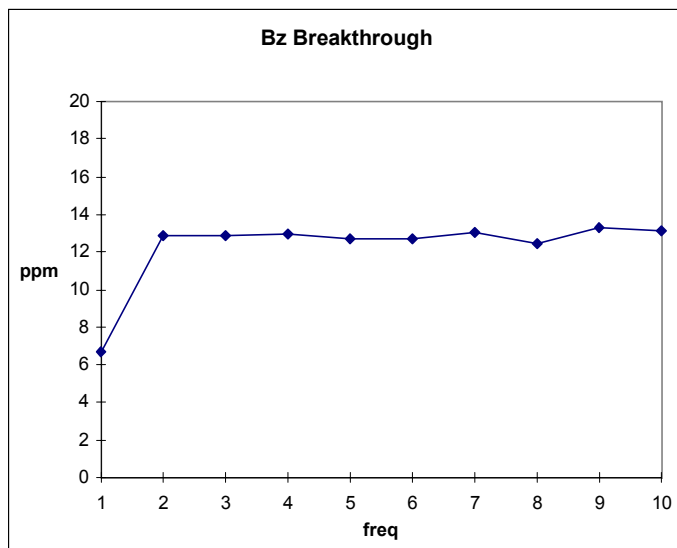


Figure 3. Breakthrough curve in a run in well KL-2RD

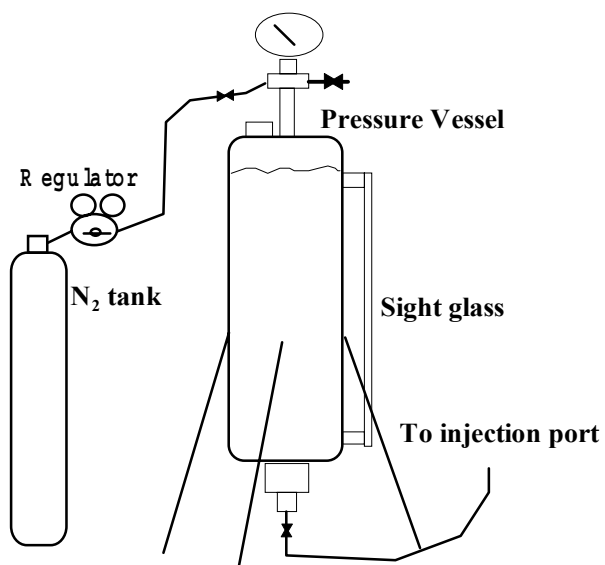


Figure 4. Injection set-up

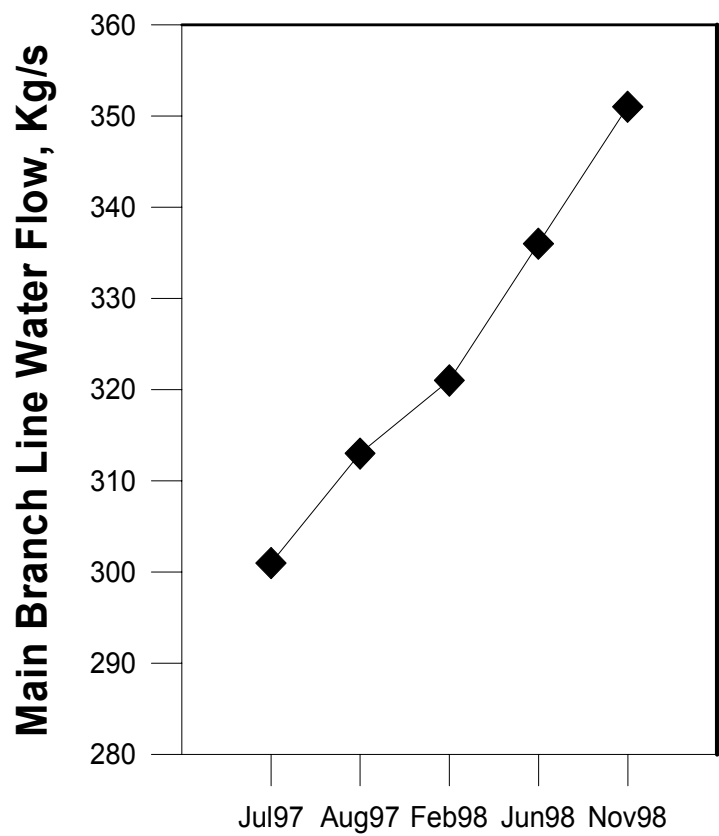


Figure 5. Water flow trend of Main Branch Line with time

Table 1. Recovery of sodium benzoate in brine

NaBz added, ppm	Actual Conc (+ background),			Recovered Conc, ppm	% Recovery
	Trial 1	Trial 2	Ave		
0	1.75	1.80	1.77		
1	3.01	2.86	2.94	1.16	116.45
2	3.83	3.85	3.84	2.07	103.36
5	6.87	6.85	6.86	5.09	101.76
10	11.80	11.98	11.89	10.12	101.19

Table 2. Comparison of HPLC and UV-Vis methods

Sample Code	HPLC	UV at 230 nm	% Difference
	ppm benzoate		
KL-1RD	14.97	15.05	0.5
KL-2RD	16.16	16.07	0.6
SK-2D	16.68	16.48	1.2
SK-4B	16.25	16.54	1.8
MT-1RD	13.60	13.78	1.3
MT-2RD	14.42	14.47	0.3

Table 3. Flow measurements at different times but same day in wells SK-4B and MT-1RD

Well	Date, 1998	Time, HHHH	WHP, kscg	Inj. flow rate, Kg/s	Inj. conc., ppm	BG conc., ppm	Plateu conc., ppm	Flow, Kg/s
SK-4B	19 Aug.	1443	9.9	0.0923	3265	2.4348	9.9839	39.9 ± 0.9
	19 Aug.	1514	9.9	0.0909	3296	2.1684	9.6833	39.9 ± 1.1
MT-1RD	13 May	1430	9.2	0.0882	16884	5.7400	16.5000	138.3 ± 2.4
	13 May	1452	9.2	0.0882	16750	5.7400	15.6000	138.4 ± 3.0

Table 4. Flow measurements at different dates in wells APO-3D, SP-4D and MT-2RD

Well	Date, 1998	WHP, kscg	WF ave, Kg/s	Remarks	% Difference
APO-3D	23 June	7.8	63.4	pressure vessel	0.5
	02 June	7.8	63.1	TFT	
SP-4D	23 June	9.8	56.8	pressure vessel	1.6
	02 June	10.2	55.7	TFT	
MT-2RD	24 June	4.6	62.6	pressure vessel	3.6
	02 June	4.6	60.4	TFT	

Table 5. SP-4D water flow trend

Date, 1998	WHP, kscg	WF, Kg/s
23 June	9.8	56
29 July	9.1	47
31 July	9.1	46
03 August	9.8	43