Comparative Review of Methylene Blue Analysis Procedures in Nag-67 Redrill, Tiwi Geothermal Field

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ABSTRACT

Methylene blue (MeB) analyses of clay samples from selected intervals of Nag-67 original hole and redrill leg were conducted during the 2016 Nag-67 redrill workover. This was done to establish local alteration patterns in the outfield Naglagbong injection sector, which is critical in determining the setting depth of the 13-3/8" casing string to ensure complete isolation of the argillic zone and guarantee adequate reservoir pressure containment.

MeB titration tests were conducted in two different sample preparations; one utilizing a heat-treated, acidified clay suspension and another using an EDTA-treated suspension. Results from the method utilizing H_2SO_4 suspensions were found to be more difficult to replicate and appear to be overestimating the smectite content. This is potentially due to several limitations in the experimental set-up, contamination of archived Nag-67OH samples and subtle differences in acid and heat treatment damaging parts of the clay structure. On the other hand, titrations of EDTA-treated suspensions provided clear and consistent endpoints.

The latter method revealed two separate smectite peaks within the clay-rich zone identified through the microscopy of rock cuttings. The peaks are encountered at 2820 – 2920 ft-MD and at 3400 – 3500 ft-MD. The interval starting from the first peak until the second smectite peak can be considered to be part of the argillic zone. From the second smectite peak at 3400 – 3500 ft-MD, the apparent surface areas of succeeding samples drop and taper off with depth, marking the increasing prevalence of more thermally-stable, non-expanding clay minerals such as illite. This signals the entry to the transition zone, and is the preferred depth for setting the bottom of 13-3/8" string.

1. INTRODUCTION

The Tiwi geothermal field is a fracture-controlled, liquid-dominated geothermal system located at the northeastern flank of Mt. Malinao, a potentially active volcano part of the Bicol Volcanic Arc, ~350 km from Manila.

The Tiwi geothermal field is operated by Philippine Geothermal Production Company, Inc. (PGPC), a joint venture between Allfirst Equity Holdings, Inc., an affiliate of SM Investments Corporation, and Chevron Geothermal Philippines Holdings, LLC. It has been in commercial operations since 1979, supplying steam to third-party-owned power plants with an installed capacity of 234 MW.

Nag-67 is an injection well part of the Southeast Hot Brine Injection System (SEHBIS), located in the outfield Naglagbong sector of the Tiwi geothermal field (Figure 1). The original well (Nag-67OH) was drilled in 1987 as a dedicated injection well and had been worked over on several occasions with scale drillouts and acidizing to regain injection capacity lost due to silica scaling. However, the last workover was not successful and it was therefore decided to re-drill the well (Nag-67RD) to regain the original injection capacity of Nag-67OH by targeting the permeable zones intersected in the existing Nag-67 well. The additional capacity would then increase the injection capacity of the Outfield Hot Brine Injection System (OHBIS) providing injection flexibility by enabling brine redistribution in the South East Hot Brine Injection System (SEHBIS).

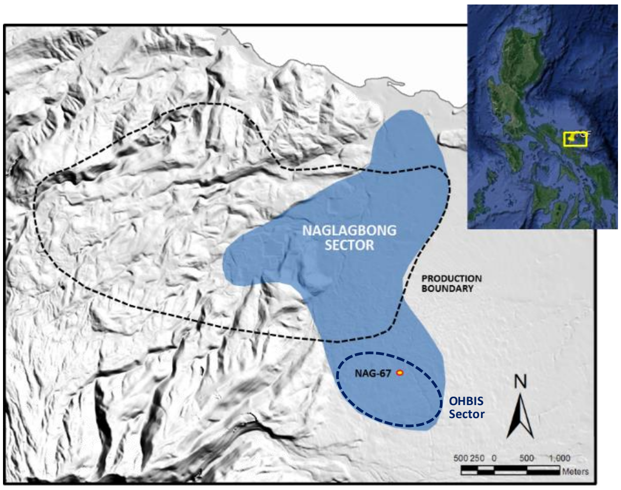

Figure 1: Location of Nag-67 and the Tiwi Geothermal Field, Luzon, Philippines

The re-drill required drilling out of the existing well casing and into the clay-cap that had been identified in the original well. Methylene blue (MeB) analyses of clay samples at selected intervals from Nag-67OH and Nag-67RD wells were conducted from March 3 to March 11, 2016 to aid in identifying the existence of swelling clays in Nag-67RD while drilling. Methylene blue (MeB) is a quick and inexpensive technique used to provide smectite clay content estimates and trends in geothermal well cuttings. Clay content is a critical information during drilling as it is used as one of the indicators in setting the casing shoe of the well. Smectite concentration typically peaks within the smectite-dominated argillic zone and, in turn, the MeB response is expected to reach maximum value in this section. Once the smectite interlayers with illite (transition zone) with increasing depth and temperature, the smectite content decreases corresponding to a decrease in the MeB trend.

The potential use of methylene blue adsorption as a field technique for the identification of swelling clays in cores and cuttings from geothermal wells was first introduced to PGPC through a report by Harvey (1994) and succeeding work by Gunderson, et al (2000). However, MeB analysis was first used in Mak-Ban during the drilling of Bul-103 to Bul-113 in 2000-2004 while in Tiwi it was first utilized during the drilling of Bar-11 and Kap-35 in 2008-2009. The method proved to be useful and effective, when used in conjunction with other drilling data, in determining viable casing shoe depths.

2. METHODOLOGY

There are two standard MeB sample preparations followed by PGPC (Vicedo, 2008) – the first uses a heat-treated, H_2SO_4-acidified clay suspension while the other utilizes a Na_4EDTA-treated suspension. The former requires boiling the suspension under a range hood, limiting the conduct of the analysis inside a laboratory since it poses safety risks if conducted elsewhere due to acid handling and boiling. It is thus not normally conducted at the rig site.

2.1 Sample Preparation

Rock cuttings are collected in 20-foot intervals. Excess bentonite is washed off and the samples are dried for one hour in a 100°C oven. The dried rock cuttings are ground into a fine powder and are weighed accordingly to create the clay suspensions.

To make the acid suspensions, 15-mL of 2N H_2SO_4 is added to 0.20 to 0.50-g samples of the ground rock samples. The suspensions are then subjected to heat treatment by gently boiling them for two minutes (Harvey, 1994).

For the EDTA method, ground rock samples are first suspended in distilled water to create 2-5% clay suspensions (by weight). For every gram of dried sample, 10-mL of 10% Na_4EDTA is added to the clay suspensions (Figure 2A). The titration is then performed on a 10-mL aliquot taken from this main suspension.

2.2 MeB Titration and Calculations

The titration procedure uses a standard 0.1M methylene blue solution. The procedure is essentially similar for both the H_2SO_4 and Na_4EDTA-treated suspensions where a drop of the titrated suspension is blotted onto a filter paper (Whatman's No. 1 or 40) for every stepwise addition of methylene blue. For the H_2SO_4 suspensions, MeB is added in 0.2-mL increments while for Na_4EDTA-treated suspensions, it is added in 2.0-mL increments.

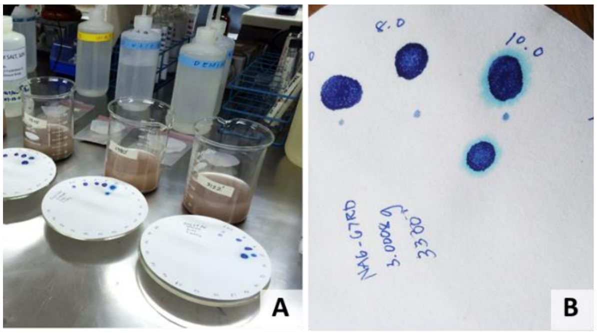

Figure 2: (A) EDTA-treated clay suspensions prior to MeB titration. (B) Blot test results of Nag-67RD 3300 ft-MD sample prior to and at the endpoint of titration

This is done until the apparent endpoint is reached, characterized by the development of a light blue halo radiating from the central dark blue blot (Figure 2B). Upon reaching this point, the titrated suspension is mixed for two minutes and the blot test is conducted again. The persistence of the light blue halo indicates that the true endpoint has been reached. However, if the repeat test returns a clear corona, the titration is continued.

Equations 1 and 2 relate the amount of MeB used to the amount of smectite in the sample. The former is used in acid suspensions (Harvey, 1994), while the latter is for EDTA-treated samples (Reyes, 1995).

$$\%\,Sm = 3 \times \left(\frac{V_{MeB}}{g\ sample}\right) \tag{1}$$

$$ASA = 6.45 \times \left(\frac{V_{MeB}}{g\ sample}\right) \tag{2}$$

Unlike the H_2SO_4 method, which has been calibrated to yield the % smectite, the Na4EDTA-based MeB procedure gives the apparent surface area (ASA) of swelling clays in the sample. The ASA is a calculated parameter that is based on the total cation-exchange capacity of the sample, which has some degree of equivalence with the amount of smectite in the sample.

3. RESULTS

3.1 H_2SO_4 Method

Results of the MeB tests for Nag-67OH and RD are summarized in Tables 1 and 2, respectively.

Table 1: Results of Nag-67OH MeB Analysis (Acidified Suspension) and Lithologic Log Identification

Interval (ft-MD)	% Smectite	Alteration Zone[1]	Alteration Intensity[1]
2420 - 2440	44	Argillic	Strong
2420 - 2440	54	Argillic	Strong
2840 - 2860	28	Argillic	Strong
2940 - 2960	66	Argillic	Strong
3100 - 3120	115	Argillic	Weak

[1] Qualitative descriptions based on Nag-67OH lithologic log

Table 2: Results of Nag-67RD MeB Analysis (Acidified Suspension) and Visual Estimates of Smectite

Interval (ft-MD)	% Smectite	Visual Estimates
2860	34	30
2900	103	40-50
2900*	63	40-50
2920	57	No Sm
3122	72	20-30

* Confirmatory run

Methylene blue tests following the H_2SO_4 procedure yielded largely variable smectite content estimates, and in some instances, anomalously high values. Anomalous smectite concentrations were noted in samples from 3100 ft-MD in Nag-67OH and 2900 ft-MD in Nag-67RD where smectite content estimates are 115% and 103%, respectively. Repeat tests of the Nag-67RD 2900 ft-MD sample yielded 63% smectite

Comparing the methylene blue test of original hole and redrill cuttings, it was observed that downhole smectite concentration trends for both OH and RD vary considerably with depth (Figure 3). Qualitative descriptions of the 2420 – 2440 ft-MD, 2840 – 2860 ft-MD and 2940 – 2960 ft-MD intervals indicated that these sections are weakly argillized. However, MeB smectite estimates yield relatively high concentrations at 44%, 28% and 58%, respectively. It is important to note, however, that these samples have been in storage for three decades and have been subjected several, sporadic location transfers, mainly due to typhoon damages on sample storage facilities. The impact of these on sample reliability and integrity could not be discounted and could explain the source of the discrepancy observed.

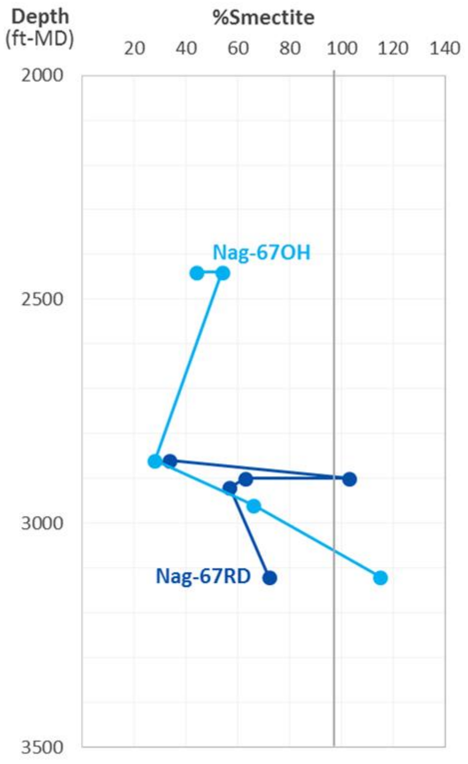

Figure 3: Nag-67OH and RD Smectite Concentration v. Depth

Slight variations in the method also produces slight differences in smectite estimates. Differences in heat treatment was shown to vary the results of the titration considerably. Gently heated samples from Nag-67OH 2900 ft-MD registered 54% smectite, as compared to the boiled samples where only 44% was recorded.

3.2 Na_4EDTA Method

Results of MeB runs using EDTA-treated clay suspensions showed clear and consistent endpoints. Comparing the results of MeB tests from both Nag-67OH and RD, intervals from 3420 – 3440 ft-MD showed consistent ASA values of 31 and 30-m^2/g, respectively. In addition, Nag 67OH 3480 ft and Nag-67RD 3480 ft also showed comparable values at 30 and 34-m^2/g, respectively.

Methylene blue analysis revealed the presence of a smectite-rich horizon in the shallow portion of the borehole. A first peak was encountered at depths of 2820 – 2920 ft-MD, where a peak ASA of 37-m^2/g was detected. This value rapidly dips down before hitting the second peak at 3400 – 3500 ft-MD with a peak ASA of 47-m^2/g at 3440 ft-MD. Confirmatory runs were performed in this interval to ascertain the high ASA values. Repeat tests return an ASA of 40-m^2/g, confirming the abundance of smectite in this zone. After this peak, calculated ASAs drop and taper off. Below 3780 ft-MD, recorded ASAs are generally low ranging from 4 to 17-m^2/g (Figure 4).

Table 3: Results of Nag-67RD MeB Analysis (EDTA-treated Suspension) and Visual Estimates of Smectite from Microscopy

Interval (ft-MD)	% Smectite	Visual Estimates
2799	4	
2821	37	
2880	26	30
2900	30	40-50
2920	26	
2980	21	10-20
3122	17	20-30
3122*	21	20-30
3180	13	10-20
3200	17	20-30
3300	22	20-30
3360	30	
3400	30	10-20
3400*	30	10-20
3440	47	20-30
3440*	41	20-30
3460	30	30
3480	34	
3500	21	20
3560	15	
3600	17	
3600*	17	
3700	22	
3780	4	5-10
3900	9	5
4000	13	<5
4100	9	5-10
4200	9	
4300	4	10
4440	13	5-10
4500	17	
4560	13	
4640	13	5-10
4640*	13	5-10
4740	17	

* Confirmatory runs

4. DISCUSSIONS

4.1 MeB Procedure Comparison

Comparing the two sample preparations for MeB titration in terms of replicability and comparability with other estimates, there is a slight advantage in using Na_4EDTA-treated suspensions over the acid suspensions.

While not entirely comparable, general trends of smectite content based on microscopic visual estimation better match downhole MeB trends obtained through the titration of EDTA-treated suspensions. Visual estimates from microscopy show that the smectite-rich zone ranges from the kickoff depth to 3600 ft-MD, constituting 20% to 50% of the sample by volume. Further below, poorer concentrations were observed from 3800 to 4740 ft-MD with only 5-10% smectite by volume. This trend is also reflected in the apparent surface areas calculated for the samples from these depths, with samples from 2800 to 3500 ft-MD having ASAs of 10 to 47-m^2/g in contrast with the samples from the 3800 to 4740 ft-MD interval, with calculated ASAs of only 4 to 17-m^2/g (Figure 4).

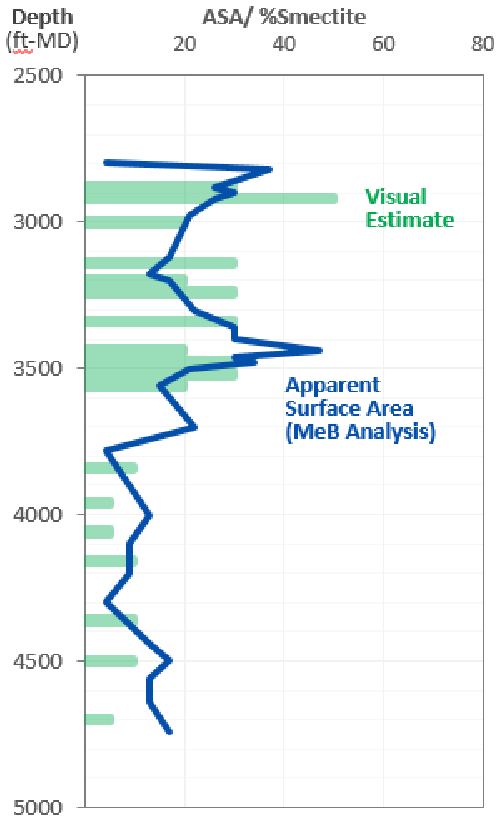

Figure 4: Downhole estimates of smectite concentration from cuttings microscopy and methylene blue analysis

Aside from being comparable to visual estimates, MeB runs using EDTA-treated suspensions are also easily replicated, with clear and consistent endpoints unlike in acidified samples, where the endpoints are more difficult to replicate in parallel runs.

There is also the issue of potential overestimation of smectite concentrations in samples using the acid suspensions. Smectite contents above 100% observed at 2900 ft-MD (Nag-67RD) and 3100 ft-MD (Nag-67OH) could indicate that the calibration factor may need to be revisited.

Minor deviations in the methodology also has a large impact in smectite estimates – with an observed 10% difference in samples from Nag-67OH 2900 ft-MD for samples subjected to boiling and gentle heating. Currently, differences in the % smectite calculated can be credited to differences in acid and heat treatment techniques.

Mathers, Weed and Coleman (1954) noted that increasing the severity of acid treatment resulted in partial decomposition of the clay shown by the loss of Fe, Al and Mg from the clay lattice. This results in decreased cation exchange capacities causing decreased smectite concentrations for the boiled sample (Figure 5).

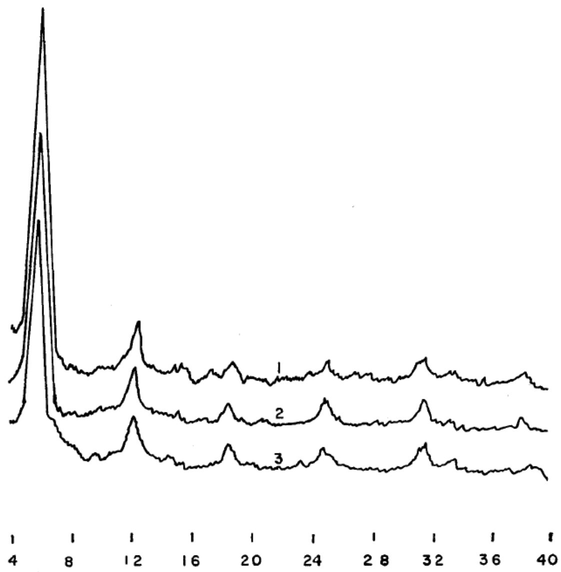

Figure 5: X-ray diffraction patterns of HCl-treated smectites at (1) 3% HCl at 30°C, (2) 3% HCl at 80°C and 10% HCl at 80°C (Mathers, Weed and Coleman, 1954).

4.2 Clay Cap Characterization

Downhole ASA trends were able to further resolve the smectite-rich zone into two high smectite horizons at 2820 – 2920 ft-MD and 3400 – 3500 ft-MD. The two zones are separated by a silicified zone, marked by the abrupt appearance of significant quantities of quartz.

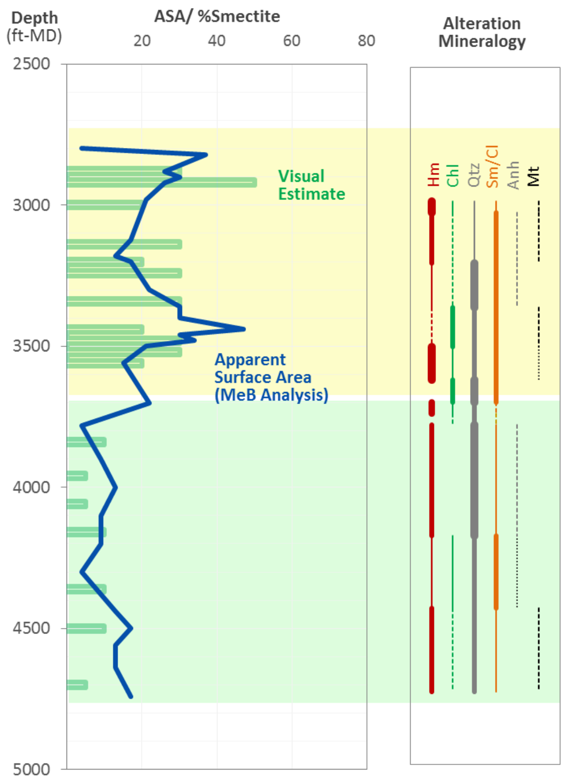

Figure 6: Correlation between smectite concentrations and alteration mineralogy. Argillic alteration zone is highlighted in yellow.

The peak at 2820 – 2920 ft-MD until the second smectite peak can be considered to be part of the argillic zone. This is consistent with microscopic observations of abundant smectite. The ASA of samples succeeding the second smectite peak at 3400 – 3500 ft-MD drops off and the ASA trend tapers off with depth, signaling the beginning of the transition zone. Visual observations of smectite show that it is mostly a minor mineral below these depths (Figure 6).

The end of the argillic zone, pegged at 3700 ft-MD based on smectite apparent surface area and alteration mineralogy, is then regarded as the minimum setting depth for the 13-3/8" casing.

5. CONCLUSIONS

The results of Nag-67 methylene blue analysis re-affirm the effectiveness and reliability of the Na_4EDTA-based method compared to the sulfuric acid-based MeB method. The team is recommending to continue utilizing the Na_4EDTA-based MeB method in the future drilling campaigns in both Tiwi and Mak-Ban.

In addition, the Na_4EDTA-based method was able to define two smectite peaks in Nag-67RD: at 2820 – 2920 ft and at 3400 – 3500 ft. The first peak is characterized by ASA ranging from 37 to 21 whereas the second peak ranges from 21 to 47. The rest of the smectite trend shows lower ASA's than these.

Based on the Na_4EDTA method, the argillic zone is determined to range from 2820 – 3500 ft-MD. After the second smectite peak, there is a decreasing trend in the calculated ASA. This drop in ASA is interpreted to be where the smectite in the argillic zone transitions to the more thermally stable, non-expanding interlayered clays of the transition zone.

Table 4: Comparison of Advantages and Disadvantages of using Methods 1 and 2.

Method	Advantages	Disadvantages
H_2SO_4 Method	• Returns % smectite content and can be readily compared to smectite estimates	• Overestimates % smectite content • More sensitive to slight changes in experimental set-up • Special facilities are needed to conduct the test at the rig site • Safety risk (acid handling)
Na_4EDTA Method	• Establishes smectite content trend • Provides reliable smectite trend • Can be done at the rig site (minimal time delay in getting the result) • Lower safety risk (does not involve handling of acid) • Historically, an effective guide in casing shoe setting depth in the previous drilling campaigns	• Could not be compared to WSG % smectite estimates, instead, trends are compared.

6. RECOMMENDATIONS

Further studies need to be conducted in order to resolve the potential overestimation issue found in using the acidified suspensions. This can be resolved by using a parallel analytical technique to resolve actual smectite concentrations in our clay samples (e.g. XRD – Rietveld method; BET gas adsorption, UV-Vis spectroscopy) and recalibrating the MeB amount with these values. The Na_4EDTA method can also benefit from this through the calibration of the ASA with known smectite concentrations.

MeB titration increments could also be reduced further to improve the resolution of the test, especially for the detection of small changes in smectite concentrations among different sampling intervals.

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