Genesis of Smectite Scales in Mindanao Geothermal Production Field, Philippines

Rosella G. Dulce, Gabriel M. Aragon, Lauro F. Bayrante and Benson G. Sambrano

Energy Development Corp., Merritt Road., Fort Bonifacio, Taguig City, Philippines

dulce.rg@energy.com.ph

Keywords: Smectite, scale, saturation index, deposits, brine

ABSTRACT

Smectite [$Al_4Si_8O_{20}(OH)_4n{\bullet}H_2O$], a hydrated expanding clay mineral is present in significant amounts in the surface facilities of the Mindanao Geothermal Production Field (MGPF). It is the dominant constituent of total deposits in the Low-pressure (LP) Flash Vessel Station, and Separator Vessels (SV) 1A and 1B. It is found in minor quantities of total deposits downstream of these vessels. The fragmental clay deposits cause recurrent operational problems such as flooding of brine surge tank and flash vessel, clogging of pump at the LP station, and subsequent MGPF plant trip.

Petrologic and scanning electron microscopy (SEM) analyses of clay samples reveal micro-textural features and mineral association suggesting that they deposited directly from the brine in the surface facilities, and are not hydrothermal alteration minerals from production wells. Moreover, simulation using SV-1A/1B brine chemistry gives a high saturation index of smectite (log Q/K of 10-24) indicating high potential for depositing smectite. Very high saturation index is due to the brine's elevated aluminum content of 640 ppb. Thus, abundant smectite scales will likely form in SV-1A, SV-1B, and LP station where separated brine from SV-1A, SV-1B and SV-2C is further flashed at 120°C. These soft clay deposits are easily removed from the vessels and transported as fragmental solids downstream of these facilities.

Since aluminum is the major parameter that controls smectite saturation index, clay scaling may be controlled by brine treatment with Al-sequestering or complexing agent (Gallup, 1997).

1. INTRODUCTION

Smectite refers to a hydrated expanding clay mineral with a general chemical formula of $Al_4Si_8O_{20}(OH)_4n{\bullet}H_2O$ (Read, 1970). Aside from being commonly observed as a hydrothermal alteration of rock cuttings from geothermal wells, this clay mineral is noticeably present in the surface facilities of the Mindanao Geothermal Production Field (MGPF). It is abundant in the Low-Pressure (LP) Flash Vessel Station, particularly in brine surge tank, flash vessel, bypass line and valve, and pump. It occurs in lesser amounts upstream of this station: solid trap, main brine line 1 (MBL-1), brine line sampling points after SV-1A/1B and SV-2C, and at the bases of SV-1A and SV-1B. The huge amounts of fragmental clay deposits cause recurrent operational problems such as flooding of brine surge tank and flash vessel, clogging of pump at the LP station, and subsequent MGPF plant trip.

This study attempts to determine the probable origin of abundant smectite in the LP station of MGPF. Samples were collected and analyzed using polarizing microscope and SEM and energy dispersive x-ray (EDX). Brine chemistry at selected sampling locations was also studied, and simulation using WATCH speciation software was done to determine the potential of the brine to directly deposit smectite. The conduct of this study will focus on the root cause of the formation of huge amounts of smectite scales.

2. SMECTITE CHARACTERIZATION

2.1 Petrologic Analysis

Abundant fragmental sand- to pebble-sized deposits at several Fluid Collection and Recycling System (FCRS) locations in MGPF (Table 1 and Fig. 1) were collected and analyzed using a polarizing microscope. The compositions of the samples are given in Table 1, and summarized below.

1) Smectite is the dominant constituent of the total deposits in SV-1A (80%), SV-1B (55%), and MBL-1 (83%), and in the LP station in brine surge tank (85%), bypass valve (80%), and bypass line (80%).

2) Amorphous silica, on the other hand, is the dominant constituent at SV-1A sidewall, standpipe, and base (70-85%); SV-2C brine line (70%); solid trap (40%); and in the LP station at flash vessel wall (97%) and in brine line pump (90%).

3) Corrosion products generally occur in minor amounts, except at SV-1A standpipe (20%) and in the solid trap (35%) where they are present in significant quantities (20-35%).

4) Materials that come from production wells such as rock cuttings (andesite, dacite, tuff breccia, completely altered rocks and calcite grains) are present in rare amount, usually ~5%.

The abundant dark brown to black, soft materials in the collected samples are identified as smectite based on optical properties under a polarizing microscope. All smectite samples found in MGPF FCRS from SV-1A, SV-1B and SV-2C till the LP station are similar. Under the microscope, smectite is light to dark brown, or greenish to yellowish brown mineral. It has a grain size range of 0.07-7.00 mm. Smectite is present together with other fine-sized fragmental amorphous silica, corrosion products and rocks. Smectite comprises from 5% to 85% of the total deposits in MGPF FCRS.

Table 1: Sampling locations in MGPF

Sampling Location	Smectite	Amorphous Silica	Corrosion Products	Rock Cuttings
1. SV-1A sidewall	5	80	15	---
2. SV-1A stand pipe	10	70	20	---
3. SV-1A base	5	85	10	---
4. SV-1A brine line	80	6	7	7
5. SV-1B brine line	55	15	10	20
6. SV-2C brine line	3	70	15	12
7. MBL-1 (Main Brine Line)	83	2	7	8
8. Solid trap	20	40	35	5
9. Low-pressure Flash Vessel Station				
Brine surge tank base	85	5	2	8
Flash vessel wall	---	97	1	1
Flash vessel base	3	85	5	7
Bypass valve	80	8	2	10
Bypass line	80	15	---	5
Brine line pump	4	90	6	---

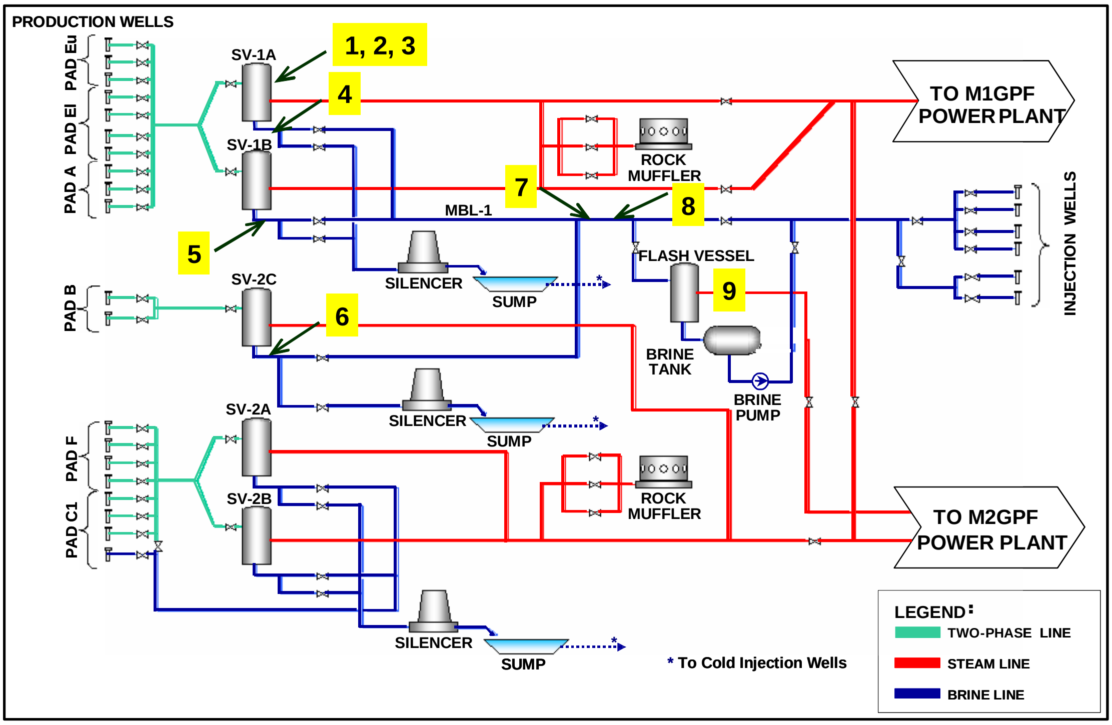

Figure 1: Process flow diagram of Mindanao geothermal production field (MGPF)

Smectite occurs commonly as rounded birefringent crystalline masses. Occasionally, it exists as amorphous to microcrystalline materials (Fig. 2). Smectite exhibits fibrous, radiated, or daisy-like textures (Fig. 3), very typical of smectite scales, but not observed in smectite as hydrothermal alteration mineral. It also shows very fine ripple marks (Fig. 2) which are displayed by amorphous silica scales in geothermal brine lines. In addition, smectite also has wavy extinction like amorphous silica. Smectite is occasionally thinly (1-2 mm) interlayered with amorphous silica and corrosion products (Fig. 4). It is embedded with abundant minute dendritic opaque minerals (Fig. 5).

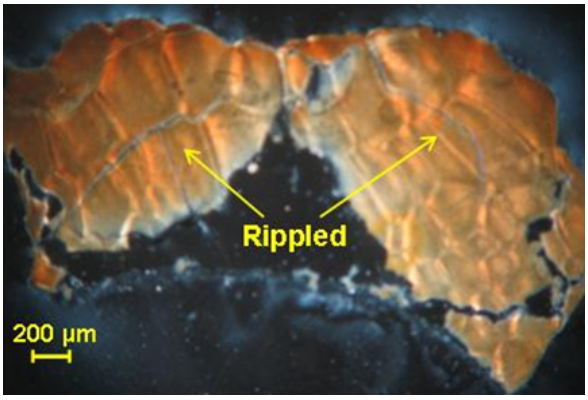

Figure 2: Amorphous brown clay showing ripple marks

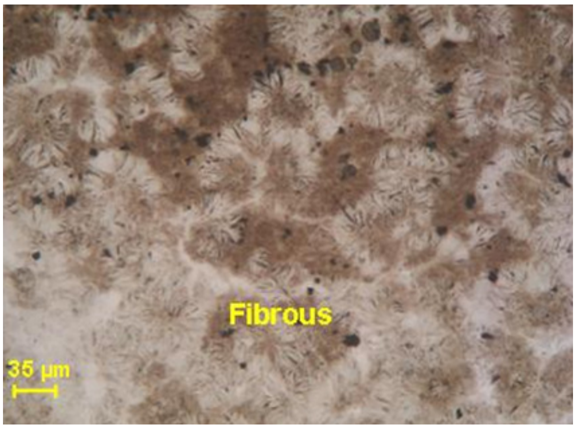

Figure 3: Fibrous, radiated texture exhibited by smectite scales

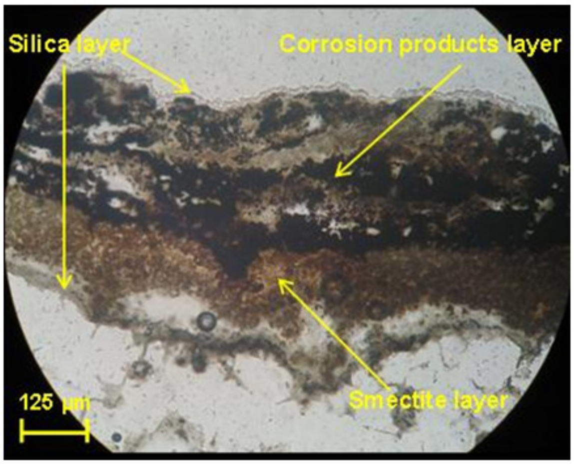

Figure 4: Smectite scales interlayered with amorphous silica and corrosion products

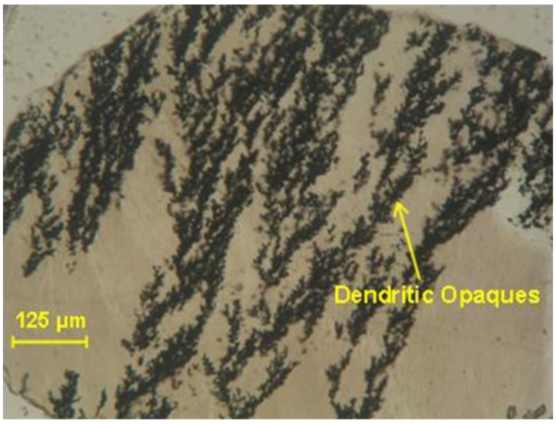

Figure 5: Very fine dendritic corrosion products embedded in smectite

2.2 Scanning Electron Microscopy - Energy Dispersive X-ray Analysis (SEM – EDX)

2.1.1 SEM Photomicrographs of Smectite Scales

Electron micrographs of smectite samples show features beyond the magnification capability of a polarizing microscope. Fine scale-like, micaceous to flaky texture is displayed by smectite samples collected from MBL-1 (Fig. 6). In photomicrographs of smectite from the brine surge tank (Fig. 7), aggregates of fine, rounded plates and globules of microcrystalline smectite are observed. These resemble photomicrographs of amorphous to microcrystalline silica. On the right side of Figures 7a and b, however, flakes of smectite indicating crystalline nature are discernible.

2.2.2 Clay Composition in Weight Percentages Based on EDX Analysis

The four samples coded Brine Surge 1, Brine Surge 2, MBL-1A and MBL-1B collected from brine surge tank and MBL-1 are composed dominantly of O_2 (~70-80 wt. %) and Si (~10-15 wt. %), and minor amounts of Na, Mg and Al (< 5 wt %). Trace to nil K, Ca, Fe, Mn, Zn and Cl are also present. In MBL-1B, however, significant amounts of Fe (~6.5 wt. %) are present in the sample. These elemental compositions are consistent with the general formula of smectite as will be discussed later.

Minor differences in two important element constituents, silicon and aluminum, are clearly seen in smectite samples collected from MBL-1 and brine surge tank. Aluminum concentration in MBL-1 samples is only 0.6-1.4 weight %, compared to 2.0-3.2 weight % in brine surge tank. Silicon is also lower in MBL-1 (12-13 weight %) than in brine surge tank (14-21 weight %).

Likewise, slight variations in the minor element constituents are noted. For example, Fe, Mg and Mn are significantly higher in the MBL-1 samples. Moreover, Zn and Cl which are present in trace amounts in MBL-1 samples are absent in brine surge tank samples.

2.3 Determining the Chemical Formulae of Clay Samples Using Atomic Percentages from EDX Analysis

Table 2 gives the compositions of the same four clay samples in atomic percent. The atomic percent is defined as the number of atoms of an element per unit volume divided by the number of atoms per unit volume of the substance containing the element. This is similar to mole fraction when the atomic percent is converted to fractional value.

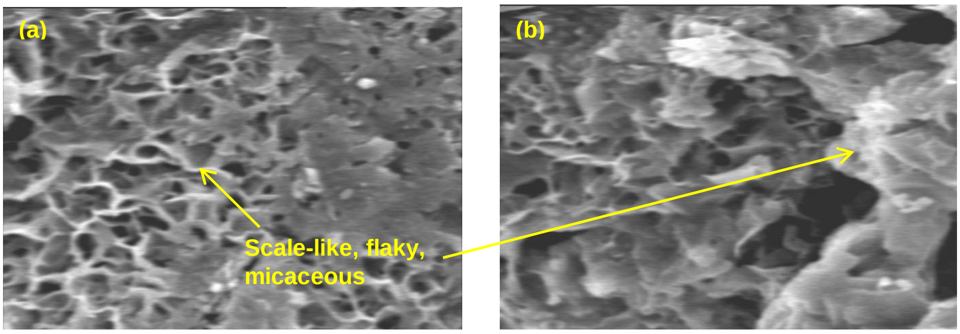

Figure 6a and 6b: SEM micrographs of crystalline smectite collected from MBL-1 show mesh-like structure (a) and flaky texture (b)

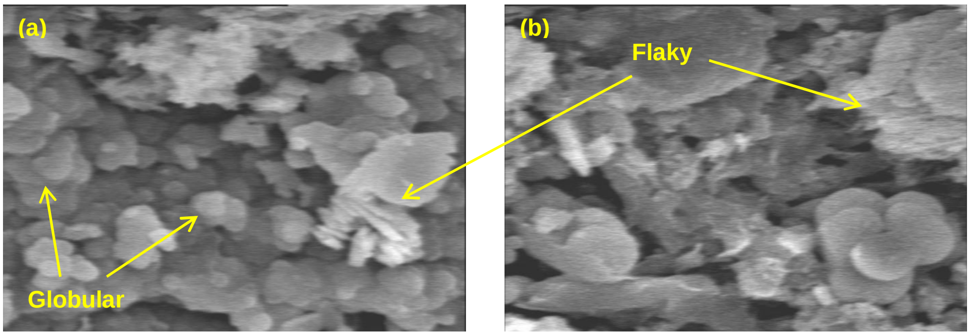

Figure 7a and 7b: SEM micrographs of smectite scales from brine surge tank exhibit aggregates of rounded plates or globules similar to amorphous silica. Flaky texture can be seen on the right side of (a) and (b).

Table 2: Compositions in atomic % of clay samples based on EDX analysis

Element	Brine Surge 1	Brine Surge 2	MBL-1A	MBL-1B
O	79.39	85.07	83.49	82.69
Na	2.08	2.08	0.83	2.37
Mg	1.79	2.30	5.34	3.31
Al	2.16	1.33	0.41	0.94
Si	13.86	8.78	8.47	7.71
K	0.26	0.07	0.09	0.15
Ca	0.28	0.15	0.15	0.23
Fe	0.19	0.16	0.75	2.15
Mn	---	0.05	0.30	0.27
Zn	---	---	0.17	0.03
Cl	---	---	---	0.14
Total	**100.00**	**100.00**	**100.00**	**100.00**

All four clay samples have been identified as smectite on a polarizing microscope. Deciphering their chemical formulae can be done using the atomic percentages. Smectite has a general chemical formula of $Al_4Si_8O_{20}(OH)_4.nH_2O$ (Read, 1970), with substitution of Mg for part of the Al. As a result of this substitution, positive ions such as Na^+ or Ca^{2+} are attached to the surfaces or edges of the minute crystals, thus balancing the negative charges which result when Mg^{2+} takes the place of Al^{3+}. In this way, variants known as sodium-smectite and calcium-smectite are formed. The positive ions (Na^+, Ca^{2+}) are exchangeable bases, and their presence accounts for the high base-exchange capacity of the mineral.

Thus, the chemical formula of smectite is slightly complex since deficiency in Al^{3+} will be directly sufficed by Mg^{2+} and indirectly by Na^+ and Ca^{2+}. The chemical formula may be in the form of $Al_wMg_xNa_yCa_zSi_8O_{20}(OH)4.nH2O$ where w, x, y and z are the subscripts for each cation. The subscript is variable and highly dependent on the availability of the cations when the clay mineral was formed.

The procedure in the determination of the chemical formulae of the clay samples is discussed in a separate report entitled "Determining the chemical formulae of clay samples from MGPF using the results of EDX analysis" (Aragon, 2006). The results are enumerated in Table 3.

Table 3: Final chemical formulae of clay samples

Sample Code	Chemical Formula for Smectite
Brine Surge 1	$Al_{2.0}Mg_{1.7}Na_{2.0}Ca_{0.3}Si_8O_{20}(OH)_4.51H_2O$
Brine Surge 2	$Al_{1.5}Mg_{2.5}Na_{2.3}Ca_{0.2}$ $Si_8O_{20}(OH)_4.69H_2O$
MBL-1A	$Al_{0.4}Mg_{4.9}Na_{0.8}Ca_{0.1}Si_8O_{20}(OH)_4.53H_2O$
MBL-1B	$Al_{0.9}Mg_{2.9}Na_{2.3}Ca_{0.2}$ $Si_8O_{20}(OH)_4.57H_2O$

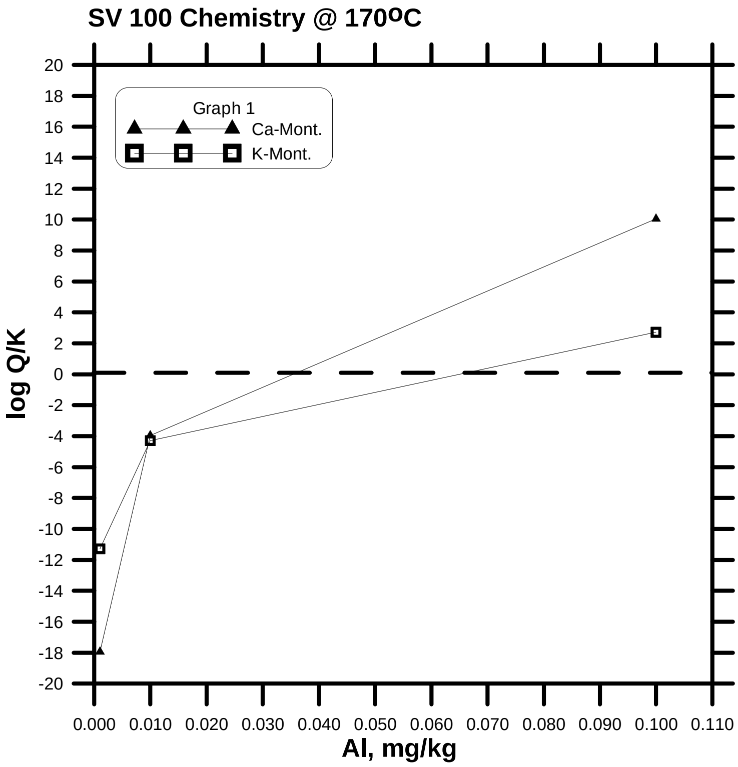

Figure 8: Aluminum concentration vs. smectite saturation index (log Q/K)

3. CLAY SIMULATION USING SV-1A CHEMISTRY

In MGPF, geothermal fluids from production wells pads E and A are directed to SV-1A and SV-1B, while discharge fluids from pad B go to SV-2C (Fig. 1). Separated brine leaving the three separator vessels pass through MBL-1 (main brine line 1). Part of this brine is diverted to low-pressure brine line (LPBL) and to a low-pressure flash vessel station. The separated brine from this second flash station is then disposed into injection wells.

Simulation of clay formation using SV-1A fluid was done using WATCH speciation program. The speciation program calculates the saturation index in terms of log Q/K of the four clay minerals: Ca-smectite, Mg-smectite, K-smectite and Na-smectite. Based on simulation, the log Q/K values at separator temperature of 170°C are ***23.8***, ***22.6***, ***9.6*** and ***10.8*** for Ca-smectite, Mg-smectite, K-smectite and Na-smectite, respectively. Thus, the brine fluid from the separator vessel is super saturated with respect to all clay minerals due to its very high aluminum content of 640 ppb. The inherently high potential for smectite deposition of the SV-1A separated brine fluid explains the presence of abundant clay minerals in the FCRS, most particularly in the second flash separator station (LP station) where the separated brine from SV-1A, SV-1B and SV-2C is further flashed at low pressure (120°C) to produce additional steam.

Sensitivity analysis was done to determine the factors controlling or promoting the deposition of the clay minerals. The following are the parameters taken into consideration (Table 4) (Urbino and Lam, 2005): Al concentration, Ca concentration, K concentration, SiO_2 concentration, pH, and boiling process. Only Ca^{2+} and Mg^{2+} were considered to represent the divalent smectite, and Na^+ and K^+ to represent monovalent smectite.

Table 4: Physical and chemical data of brine from SV-1A used for sensitivity analysis

Parameter	Data
SP, MPag	0.79
pH @ 20°C	6.92
Na, mg/kg	3462
Mg, mg/kg	0.20
Al, µg/kg	640
K, mg/kg	549
Ca, mg/kg	165
SiO_2, mg/kg	541

3.1 Aluminum Concentration

The aluminum concentration of the brine greatly affects the smectite saturation index. A minimal change in the Al concentration results to a high change in the deposition potential of the clay minerals (Fig. 8). The relationship of Al with log Q/K is almost exponential. This only shows that Al content of the fluid is a very sensitive parameter for clay deposition. At 70 ppb Al concentration, both clay minerals are above the saturation line (> 0.0). With actual Al concentration of 640 ppb, almost ten times higher, deposition of clay minerals in SV-1A fluid is indeed thermodynamically feasible. The increase in the log Q/K of Ca-smectite is higher compared to that of K-smectite, for the same amount of Al. This suggests that divalent cations smectite (Ca and Mg) are preferentially formed than the monovalent (Na and K) counterparts. Therefore, more Ca-smectite and Mg-smectite minerals are to be expected in the clay scales than Na-smectite and K-smectite.

3.2 Calcium and Potassium Concentrations

The amounts of Ca and K present in the fluid have a minimal impact on the clay saturation index (Figs. 9 and 10). Almost flat lines below the log Q/K line were obtained even with high concentrations of the divalent and monovalent cations. Thus, cation concentrations are not critical in predicting the deposition potential of clay minerals.

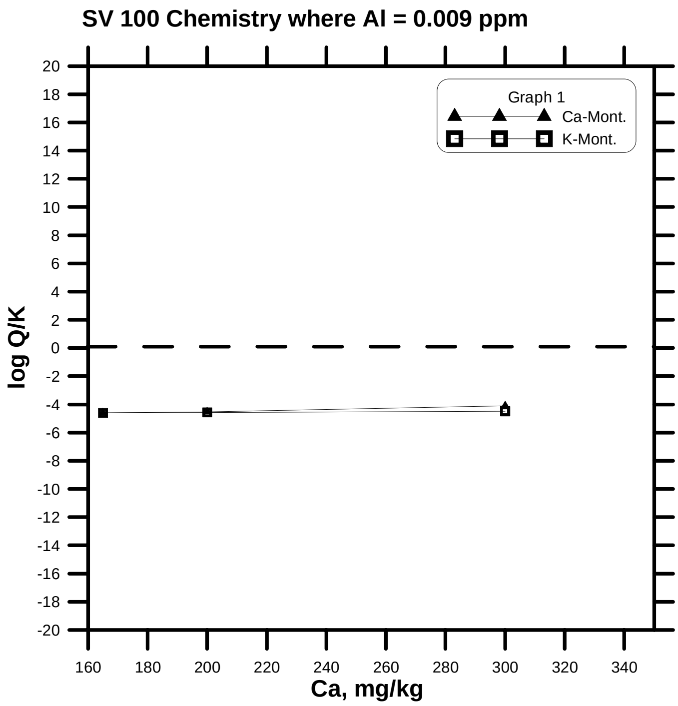

Figure 9: Calcium concentration vs. smectite saturation index (log Q/K)

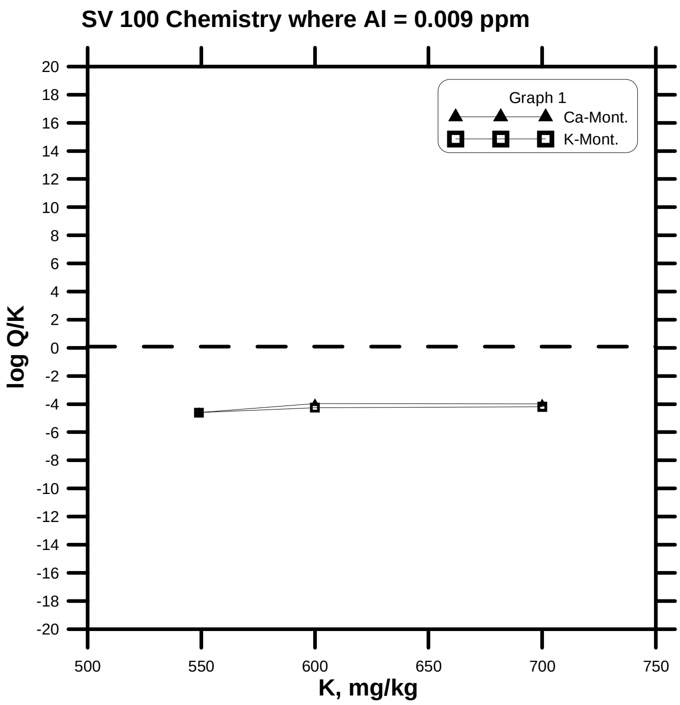

Figure 10: Potassium concentration vs. smectite saturation index (log Q/K)

3.3 Silica Concentration

Figure 11 shows that the SiO_2 content of the fluid controls clay saturation indices of both the divalent and monovalent types of smectite. This is expected since the clay minerals are silicates. Increasing the silica concentration of the fluid also increases the potential for clay mineral deposition. Again, it can be observed that the divalent type of smectite is more responsive to increases in silica concentration than the monovalent type.

It can also be seen from Figure 11 that the fluid becomes over saturated with respect to Ca-smectite at the on-set of amorphous silica saturation. Therefore, with substantial amount of Al in the fluid, already slightly over saturated with respect to amorphous silica, it is certain that divalent smectite will directly precipitate from the fluid.

3.4 pH

Figure 12 shows that the pH of the brine has an inverse relationship with the saturation index of smectite. Thus, higher saturation or higher potential for smectite deposition is expected at lower brine pH. Using SV-1A brine chemistry for the sensitivity analysis, smectite deposition is very likely at pH values of 5-6 (Fig. 12). However, the pH of the brine coming from SV-1A, SV-2C, MBL-1 and LPBL at 20°C in the laboratory is ~7, higher than this critical pH where smectite formation is predicted.

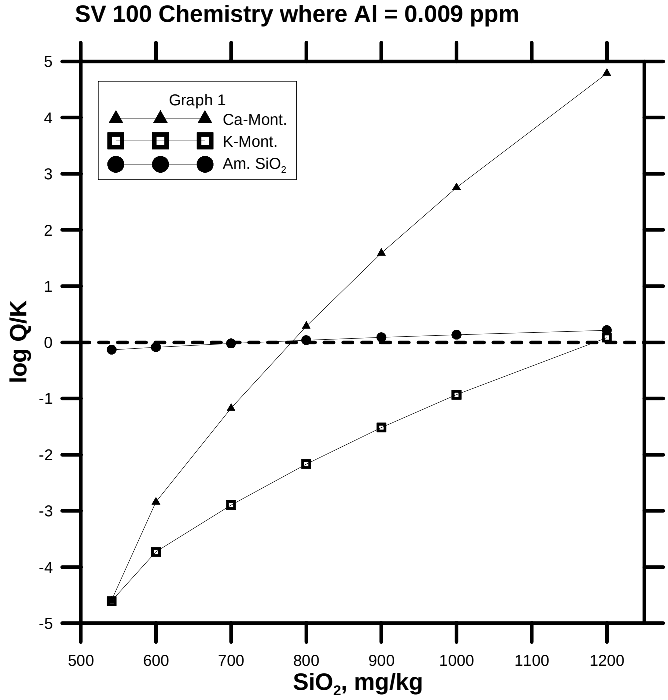

Figure 11: Silica content vs. smectite saturation index (log Q/K)

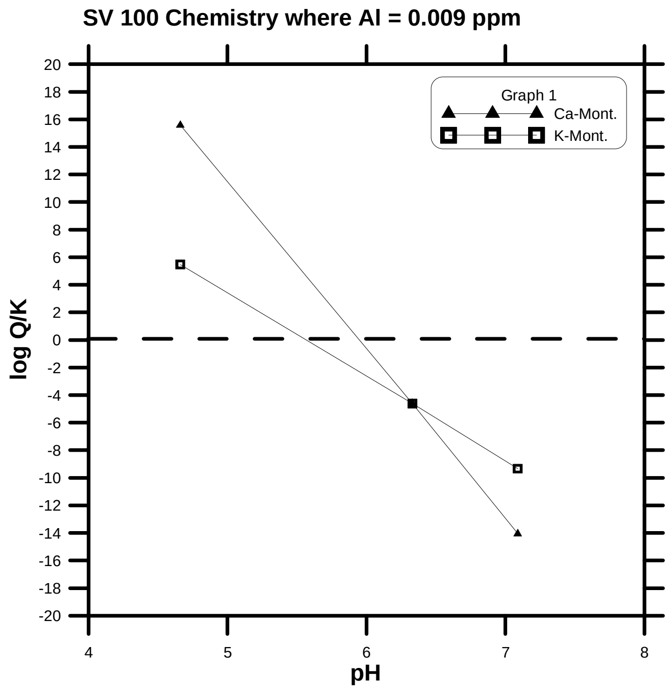

Figure 12: pH vs. smectite saturation index (log Q/K)

3.5 Boiling

Boiling or flashing process of the fluid concentrates dissolved constituents such as Al, SiO_2, Ca, Mg, K, and Na. Based on the foregoing discussions, it is expected that boiling will promote deposition of clay minerals as reflected in Figure 13. This process occurs in separator vessels SV-1A, SV-1B and SV-2C, and in the Low-pressure station, where mixed brine coming from the three separators is further flashed at 120°C. Thus, abundant smectite scales collected in the second-flash separator station and in SV-1A and SV-1B are explained by this process.

The boiling - saturation index curves of smectite minerals are linear. It can be inferred that high deposition of clay minerals will be observed with higher temperature drop. Between the divalent and monovalent types of smectite minerals, the former attains higher saturation index suggesting preferential deposition.

4. DISCUSSIONS

4.1 Interpretations based on Petrologic and SEM EDX Analyses

Smectite is the dominant constituent of the total deposits in SV-1A (80%), SV-1B (55%), and MBL-1 (83%) brine line, and in the LP station in brine surge tank (85%), bypass valve (80%), and bypass line (80%).

Smectite likely forms either inside the inspected FCRS locations. It occurs together with amorphous silica and corrosion products which are very common deposits in geothermal brine lines. Close association with corrosion products is also indicated by abundant very fine dendritic opaque minerals embedded in smectite.

Smectite samples for this study exhibit microtextures that indicate that they deposited directly from the brine in the surface facilities, and are not hydrothermal alteration minerals from production wells. Smectite samples often show good crystallinity. The fibrous, radiated or daisy-like texture exhibited by smectite is very typical of smectite scales, but not observed in hydrothermal alteration smectite. However, brown amorphous clays are still occasionally found in some samples, particularly from the brine surge tank. Good crystallinity is clearly seen in the SEM photomicrographs of MBL-1 showing smectite flakes. On the other hand, globular amorphous nature very similar to amorphous silica scales is observed in brine surge smectite samples.

It is very likely that smectite clays first deposited from the brine in the surface facilities as brown amorphous variety. With exposure of the amorphous clays to brine with time, subsequent transformation into crystalline type occurred.

Another evidence of direct formation from the brine is the layered structure of smectite. It is observed interbanded with corrosion products and amorphous silica scales. Layering of these materials suggests several deposition events or conditions that favored formation of each of the layer.

Very fine ripple mark structures shown by smectite is another proof that this mineral directly forms from a flowing fluid. As a result of this microstructure, smectite exhibits wavy extinction observed under a polarizing microscope. Ripple marks and wavy extinction are also frequently observed in amorphous silica scales.

As a hydrothermal alteration mineral of volcanic rocks, smectite occurs as light to dark brown, fibrous masses often partially or completely replacing the phenocrysts and/or the groundmass of rocks. The original rock texture or primary mineral crystal form, which it is replacing, is still discernible.

Radiated or daisy-like structure, ripple marks, and layered structure are not observed in hydrothermal alteration smectite.

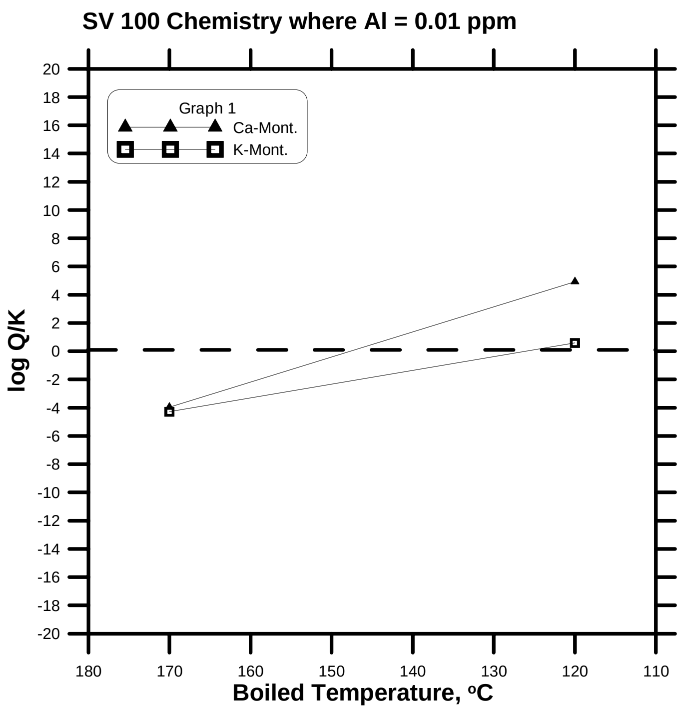

Figure 13: Boiling temperature vs. smectite saturation index (log Q/K)

4.2 Saturation Index of Smectite

The saturation index (log Q/K) of smectite, determined by clay simulation using SV-1A brine chemistry, is very high, 10-24, indicating very high potential for depositing smectite. Very high saturation index is due to the brine's elevated aluminum content of 640 ppb.

The inherent supersaturated state of SV-1A brine with respect to smectite is greatly enhanced by several factors as shown by sensitivity analysis. Aluminum concentration is the most sensitive parameter for clay deposition such that a minimal increase in Al results to an immense increase in smectite saturation index. Silica concentration also directly controls log Q/K of smectite. The Ca and K contents, on the other hand, have minimal effect on the saturation index.

Boiling or flashing of fluid concentrates dissolved constituents such as Al, SiO_2, Ca, Mg, K, and Na. Based on the foregoing discussions, this process occurring in the separator vessels in MGPF FCRS will definitely promote deposition of clay minerals (Fig. 13). Thus, based on clay simulation, smectite scales are inferred to form abundantly in SV-1A and SV-1B. These soft clay deposits are easily removed from the vessels and transported as fragmental materials downstream of the FCRS. This explains the fragmental occurrence of smectite, and not as deposits adhering to walls of surface facilities.

More abundant smectite scales collected in the LP station are explained by more smectite deposition induced by further flashing of mixed brine coming from SV-1A, SV-1B, and SV-2C at 120°C.

Ca-smectite is more responsive to increases in the concentrations of Al and SiO_2, compared to K-smectite (Figs. 8-13). Since the divalent type of smectite preferentially forms than the monovalent counterpart, more Ca- and Mg-smectite are likely present in the MGPF clay deposits than Na- and K-smectite.

5. SUMMARY AND CONCLUSIONS

Smectite [$Al_4Si_8O_{20}(OH)_4 n \cdot H_2O$], a hydrated expanding clay mineral, is noticeably present in significant amounts in the surface facilities of MGPF. It is the dominant constituent of total deposits in the LP station, and SV-1A and SV-1B, and found in lesser quantities downstream of these vessels. The fragmental clay deposits cause recurrent operational problems such as flooding of brine surge tank and flash vessel, clogging of pump at the LP station, and subsequent MGPF plant trip.

Petrologic and SEM analyses of clay samples reveal micro-textural and structural features and mineral association suggesting that they deposited directly from the brine in the surface facilities, and are not hydrothermal alteration minerals from production wells. Such microtextures are: (1) good crystallinity; (2) fibrous, radiated, daisy-structure, rarely globular and amorphous; (3) thin inter-layering with corrosion products and silica scales, minerals which are commonly found in geothermal brine lines; and, (4) very finely ripple marks and wavy extinction.

The chemical formulae of the clays based on atomic % are $Al_{1.5}Mg_{2.5}Na_{2.3}Ca_{0.2}Si_8O_{20}(OH)_4 \cdot 69H_2O$ in brine surge tank, and $Al_{0.9}Mg_{2.9}Na_{2.3}Ca_{0.2}Si_8O_{20}(OH)_4 \cdot 57H_2O$ in MBL-1. Simulation using SV-1A/1B brine chemistry gives a tremendously high saturation index of smectite (log Q/K of 10-24) indicating high potential for depositing smectite. Very high saturation index is due to the brine's elevated aluminum content of 640 ppb. Thus, abundant smectite scales likely form in SV-1A, SV-1B, and LP station where separated brine from SV-100/101/602 is further flashed at 120°C. These soft clay deposits are easily removed from the vessels and transported as fragmental materials downstream of these facilities.

REFERENCES

Aragon, G. M.: Determining the Chemical Formulae of Clay Samples from MGPF Using the Results of Energy Dispersive X-ray Analysis. PNOC-EDC Internal Report (2006).

Gallup, D. L.: Aluminum Silicate Scale Formation and Inhibition: Scale Characterization and Laboratory Experiments, *Geothermics*, **26**, (1997), 483-499.

Read, H. H.: Rutley's Elements of Mineralogy, 26th ed., c.George Allen and Unwin (Publishers) Ltd. (1970).

Urbino, G. A., and Lam, J. C.: MGPF Water Test Report. Chemistry and Isotope Laboratory Section, Geosciences Dept., PNOC-EDC Internal Report (2005).