GEOCHEMICAL CHARACTERISTICS OF ACID FLUIDS IN MT PINATUBO, PHILIPPINES

Marinela M. Buenviaje

Philippine National Oil Company-
Energy Development Corporation
Ft.Bonifacio, Manila, Philippines

ABSTRACT

The surface geochemical characteristics of Mt Pinatubo indicate widespread deep acid fluids as shown by the following: presence of solfataras or sulphur-depositing fumaroles near or at the summit, and recent or active volcanism; discharge of mixed fluids with significant chloride at middle elevations; significant amounts of sulphate found in spring discharges at almost all levels (except at lowest levels or near sea level); springs with neutral pH and high amounts of chloride and significant amounts of magnesium and boron; low Cl/Mg values accompanied by significant amounts of Mg observed at various elevations; higher proportions of gases, especially CO₂ and significant N₂; widespread occurrence of iron hydroxide deposits at almost all elevations; and all springs discharge immature waters.

A new mixing model is proposed, the Cl-B-Mg ternary diagram, to differentiate the effects on well and spring water chemistry of the following processes: seawater mixing, groundwater dilution and magmatic input.

Seawater mixing is not indicated for Mt Pinatubo springs as shown by crossplots of chloride versus other chemical constituents and the Cl-B-Mg ternary diagram. Neutral alkali chloride waters are present in the area. This is supported by the chemical crossplots, and the Cl-B-Mg plots. In the Cl-B-Mg plot, springs that discharge low pH waters are shown to be manifestations of acid fluids that are localized within a shallow or deep fault zone.

INTRODUCTION

The Mt Pinatubo geothermal area is located in the main northern Philippine island, Luzon. It is approximately 90 kms northwest of Manila.

A preliminary assessment of geothermal energy potential was done through a detailed exploration programme by the Philippine National Oil Company-Energy Development Corporation (PNOC-EDC) from 1982 to 1983 at Mt Pinatubo. The exploration programme involved semi-detailed geologic mapping, geochemical and geophysical surveys.

A three-well deep exploration drilling programme was carried out starting late 1988 at Mt Pinatubo (Fig. 1). All three wells were characterized by low pH values (2.4-3.8), excess enthalpy and low permeability.

BACKGROUND: RESULTS OF GEOCHEMICAL INVESTIGATIONS AT MT PINATUBO

Mt Pinatubo is an andesitic strato-volcano. It is the youngest and highest peak (1745 mASL) on a late Tertiary to Quaternary volcanic arc in west Luzon. A breached oval-shaped caldera is enclosing the peak of Mt Pinatubo, an andesitic dome. The caldera is formed by piece-meal subsidence due to the eruption of voluminous pyroclastic materials. The latest activity probably culminated in the growth of the dome. Structures control the location of the thermal features in this area.
The most significant geochemical characteristics of the spring and well fluids in Mt Pinatubo are summarised as follows:

Classification of springs are based on the relative Cl, HCO₃ and SO₄ contents of the water samples (Table 1). Mixed fluids with significant Cl (>20%) are found at middle elevations. Significant bicarbonate contents are found at almost all elevations. Sulphate-rich fluids are found at higher elevations i.e. discharges at greater than 1000 mASL at Mt Pinatubo.

All springs have very low to medium discharge flow rates and are below boiling temperatures. There are solfataras or sulphur-depositing fumaroles near the summit.

Chloride-rich springs such as Dagsa and Cuyucut have significant SO₄, HCO₃, and Mg. This could be due to mixing of chloride-rich fluids from depths with steam condensate fluids flowing along the flanks of the volcano. Such enrichment could also be due to mixing of acid Cl + SO₄ - rich fluids with groundwater.

The only acid spring sample is from the Pinatubo solfatara pool. The latest samples indicate that sampling points are different and show greater meteoric water contribution (M.N.Ramos, pers. comm.). Dilution with meteoric water, as indicated by lower chloride values, is observed for the most recent samples of Dangey, Lower Marunot, Kalawangan and Dagsa springs.

Iron hydroxide deposits are noted in most of the springs at Mt Pinatubo. They are normally thought of as products of weathering (P.R.L. Browne, pers. comm.). Their widespread occurrence in Mt Pinatubo are taken to be significant. Inaccuracies in sampling could account for the higher values of iron in a few samples. Acid added to unfiltered water samples would dissolve the iron hydroxide precipitates.

Higher concentrations of iron observed for the three Pinatubo wells are mainly due to acid corrosion of the wellhead assembly in drill pipes. The prevalence of iron hydroxide deposits in the surface could be linked to a significant amount of dissolved iron at depth, however.

Gas samples from the solfatara show significant amounts of H₂S but is predominantly CO₂ with some F, S₂ and Cl.

The origin of the gases discharged from wells and solfataras or fumaroles may be deduced from their chemistry. This is made possible by use of ternary diagrams - plotting relative amounts of N₂, Ar and He or CO₂ (Giggenbach and Goguel, 1982). Higher proportions of N₂ and CO₂ are indicative of magmatic origin (Figs. 2a and 2b). All the Pinatubo well discharge gases are of magmatic or volcanic origin. The solfatara or fumarole gas samples show significant air contamination.

The neutral pH of springs is due to the interaction of acid fluids with the host rocks as it travels to the surface. The very high SO₄ concentration is due to disproportionation of SO₂ into sulphuric acid and hydrogen sulphide, and the oxidation of H₂S in the vadose zone, as shown by the following reactions:

\[ \text{SO}_2 + \text{H}_2 = \text{H}_2\text{SO}_3 \]
\[ 4\text{H}_2\text{SO}_3 = 3\text{H}_2\text{SO}_4 + \text{H}_2\text{S} \]

Low Cl/Mg values and high Mg values are indicators for acid fluids. Lowest Cl/Mg values are found in Pajo and Upper Marunot.

NEAR SURFACE MIXING RELATIONSHIPS

A series of chemical crossplots (Figs. 3a-3f) of chloride versus other chemical constituents.
(Arnórsson, 1985) confirm mixing of alkali-chloride fluids with various thermal waters and dilution with meteoric waters in the Mt Pinatubo area. Springs at higher elevations show mixing of steam-heated groundwaters and thermal fluids followed by dilution with meteoric waters (Fig. 3b). Springs at different elevations show mixing of thermal fluids (including steam-heated groundwaters) (Figs. 3a, 3c and 3e) or just plain dilution with meteoric waters (Figs. 3d and 3f). Lines to indicate mixing with seawater is precisely drawn in every diagram. Seawater mixing is not indicated for springs since the mixing and dilution lines do not coincide with the line for seawater mixing.

Alkali chloride waters in Mt Pinatubo are diluted and appear at Nacoleol springs. They are mixed with other thermal waters and appear at Asin, Cuyucut and possibly at Dagsa springs. They are diluted and appear at Lower Marunot and Mamot springs.

**ORIGIN OF FLUIDS AND DEEP PROCESSES**

Very high temperatures allow for the leaching of boron from rocks and boron is volatilized into ascending steam. The Cl-Li-B ternary diagram (Giggenbach and Goguel, 1989) shows that Mt Pinatubo well fluids reflect the deep processes and a dilution line can be drawn towards Pinatubo springs.
Other Philippine wells have variable chloride and boron values (Table 2).

The relative Cl, Li and B contents of the springs, with the exception of Upper Marunot and Dagsa springs, plot them near the chloride corner but no clear distinction is made for seawater mixing from magmatic input.

As fluids start to ascend, water-rock interaction occurs, the intensity being dependent on the volume of fluid reacting with the rocks. Most of the spring and well discharge data points plot in areas of geothermal waters (Fig. 5). Surprisingly, the highly acidic Pinatubo well fluids do not plot near the Rb corner, which is supposed to imply initial dissolution of crustal rocks in acid waters formed through absorption of magmatic vapour into the deeply circulating ground water (Giggenbach and Goguel, 1989). Most of the fluids show equilibration with rocks either at depth (from well chemistry data points) or at the surface (from spring chemistry data points).

An attempt was made to differentiate the effects on well and spring water chemistry of the following processes: seawater mixing, groundwater dilution and magmatic input. Relative Cl, B and Mg contents of various springs and well waters were plotted along with seawater and solfatara spring samples (Fig. 7). Seawater has significant amounts of Cl and Mg but low boron concentration (Table 1). Volcanic springs have similar levels of Cl and Mg but contain more boron, e.g. Pinatubo solfatara spring. High temperature volcanic steam volatilizes boron from rocks and deposits it into shallow aquifers that feed springs.

Neutral pH geothermal systems (Wairakei and Tongonan wells) plot along the common Cl and B axis since their deep well fluids contain trace amount of Mg (Table 2). Brine fluids, (Salton Sea well) plot near the Cl corner along this same axis. Sedimentary-hosted geothermal systems (Ngawha well) (K. Nicholson, pers. comm.) plot near the B corner along

RESERVOIR CONDITIONS

When fluids at reservoir depths have equilibrated then the corresponding spring chemistry could be used to determine the minimum temperatures at that depth. This is done by plotting relative Na, K and Mg contents of various spring and well discharges in the area (Fig. 6) (Giggenbach, 1988). PIN-1 (acetic NaCl-SO4 fluid) and PIN-3D (acetic NaCl fluid) plot in the partial equilibrium area together with the acidic well CN-2D, and near neutral pH well 402. The neutral pH surface springs at Mt Pinatubo plot along a mixing line and yield a minimum reservoir temperature estimate of 210°C which is way below the maximum measured downhole temperature of 336°C at PIN-2D. Acidic wells PIN-2D (Na+K-Cl+SO4 fluids) and BN-3 plot near the rock dissolution line in the area for immature waters (Giggenbach, 1988).
this same axis. Vapour-dominated systems (Kamojang well) also plot near the B corner but has significant Mg due to acidic steam leaching.

Increasingly acidic geothermal wells plot away from the common Cl and B axis towards the Mg corner. BN-3 and Matsukawa wells plot quite near the B corner and have low amounts of Cl and Mg. Their acidity may be due to the presence of a higher proportion of gases and downward percolating acid fluids formed in steam-heated near surface aquifers. Pinatubo wells and the Bacman I1 well CN-2D have relatively greater proportions of Cl and variable amounts of B and Mg. Their chemistry implies deep seated acidity. Their high Cl contents are not due to seawater mixing as they contain significant amounts of boron.

"Path lines" are drawn from the neutral alkali chloride systems in the common Cl-B axis towards the volcanic systems data points. The nearer the well data points to the volcanic systems, the greater the magmatic input. A neutral alkali chloride reservoir possibly exists at the Mt Pinatubo geothermal area as deduced from the position of the well and Pinatubo solfatara data points. This is supported by the presence of a group of neutral pH springs at the lowest elevation, namely, Nacolcol springs.

The rest of the Mt Pinatubo springs show greater Mg concentration at higher elevations. Significant meteoric water component is implied for Upper Marunot and Dagsa springs. Lower Marunot spring waters come from the dilution of PIN-2D type fluids with meteoric water. Kalawangan spring waters lie along a potential "path-line" and together with Cuyucut springs (Fig. 7) are the only indicators for widespread deep acid fluids at Mt Pinatubo.

Curves are drawn between the waters near the Mg corner and the Cl-corner. These curves may represent mixing of alkali chloride waters that feed Nacolcol spring and acid (but have undergone neutralisation due to water-rock interaction) waters that feed Upper Marunot and Dagsa. The Pinatubo wells represent the dominantly acid waters that have not yet undergone neutralisation by water-rock interactions at depth (Fig. 7).

Springs that discharge acidic waters are shown to be manifestations of acid fluids that are not widespread within the reservoir (Fig. 8). This is well illustrated by the springs of Biliran geothermal project, where, out of 3 wells drilled, one well discharged acidic fluids. Though magmatic input is invoked it is mostly due to acidic steam-heated groundwaters percolating downwards through fault zones.

The Lake Nyos sample has been used to represent slightly acid CO₂-rich waters in a volcanic setting (Giggenbach and Goguel, 1989) and seawater mixing is exemplified by Morere spring, New Zealand.

The trends discussed above are summarised below (Fig. 9). The uncertainties of the mixing model come basically from assuming "representative" data points from various hydrothermal systems.
CONCLUSIONS: Geochemical Signatures of Widespread Deep Acid Fluids in Mt Pinatubo

The surface geochemical characteristics of widespread deep acid fluids at Mt Pinatubo are summarised as follows:

1. Presence of solfataras or sulphur-depositing fumaroles near or at the summit and recent or active volcanism.

2. Discharge of mixed fluids with significant chloride at elevated grounds.

3. Significant amounts of sulphate found in spring discharges at almost all levels (except at lowest levels or near sea level).

4. Springs with neutral pH and have high amounts of chloride (that is seawater mixing) and significant amounts of magnesium and boron.

5. Low Cl/Mg values accompanied by significant amounts of Mg observed at various elevations.

6. Higher proportions of gases, especially N\textsubscript{2} and CO\textsubscript{2}.

7. Widespread occurrence of iron hydroxide deposits at almost all levels.

8. Most of the springs are immature waters and a few are partially equilibrated.

Using a Cl-B-Mg diagram, Kalawangan and Cuyucut springs are seen to indicate deep acid fluids at Mt Pinatubo. Mixing lines or curves indicate that neutral alkali waters that feed Nacolcol spring have mixed with widespread acid fluids that have neutralised and are feeding Upper Marunot and Dagsa springs. Acidic springs from other hydrothermal areas are shown to be manifestations of acid fluids that are localized within a shallow or deep fault zone.

ACKNOWLEDGEMENTS

The writer wishes to thank the PNOC-EDC management for the data and facilities used in preparing this report. Special thanks to Profs. K. Nicholson, P.R.L. Browne, J.R.Ruaya and Mr. A.S.J. Baltasar for their advice and review. This report is part of the project for Diploma in Geothermal Energy Technology held at the Geothermal Institute, University of Auckland, New Zealand.

REFERENCES


### TABLE 1: CHEMISTRY OF MT PINATUBO SPRINGS AND SEAWATER

| SOURCE | ELEV. | SAMPLE | FIELD | LAB. | Li | Na | K | Mg | Ca | Fe | Cl | SO4 | F | B | Al2O3 | HCOS |
|--------|-------|--------|-------|------|----|----|---|----|----|----|----|----|----|---|---|-------|------|
|        | (mgl) | (yrmmd) | (C) |     |    |    |   |    |    |    |    |    |    |   |   | (in mg/kg) |      |
| PINATUBO | 1150 | 830515 | 58 | 1.00 | 10.5 | 10134 | 2276 | 5.84 | 2.02 | 4 | 1056 | 0.01 | 34053 | 40600 | 0.02 | 453 | 0.06 |
| U. MARINDU | 1075 | 821012 | 76 | 7.75 | 0.12 | 58 | 13.5 | 0.11 | 196 | 35.5 | 0.25 | 477 | 71 | 322 | 0.02 | 453 | 0.06 |
| DANSEY | 965 | 800514 | 41 | 7.97 | 0.41 | 112 | 0.3 | 0.04 | 129 | 46.1 | 0.11 | 77 | 322 | 0.02 | 453 | 0.06 |
| L. MARINDU | 900 | 800522 | 39 | 7.99 | 0.27 | 68 | 6.1 | 0.11 | 193 | 64.3 | 3.95 | 44 | 198 | 0.39 | 5.5 | 111 | 62 |
| MARGOT | 900 | 800403 | 50 | 7.94 | 0.38 | 157 | 14.9 | 0.06 | 6 | 62.7 | 0.27 | 265 | 260 | 0.47 | 12.2 | 157 | 165 |
| KALAMANTAN | 675 | 830511 | 38 | 7.87 | 1.34 | 785 | 62.5 | 0.15 | 1.17 | 303 | 47.4 | 0.21 | 174 | 417 | 0.17 | 5.4 | 104 | 53 |
| PULA | 675 | 800523 | 40 | 7.84 | 1.09 | 570 | 49.2 | 0.13 | 0.03 | 114 | 47.2 | 0.38 | 950 | 247 | 0.11 | 12.0 | 112 | 458 |
| PAID | 518 | 820102 | 27 | 7.27 | 0.12 | 3 | 3.8 | 0.12 | 13 | 9.2 | 0.15 | 7 | 23 | 0.02 | 0.4 | 94 | 71 |
| CUYUCUT | 495 | 820102 | 23 | 8.03 | 0.12 | 17 | 9.3 | 0.12 | 9 | 34 | 19.5 | 0.12 | 9 | 34 | 0.02 | 0.4 | 94 | 71 |
| DAGSA | 325 | 820513 | 44 | 7.99 | 2.70 | 1867 | 123.9 | 0.58 | 0.43 | 197 | 43.5 | 3.65 | 2304 | 308 | 0.11 | 27.7 | 152 | 1334 |
| ASIN | 300 | 800514 | 48 | 8.10 | 3.45 | 2170 | 148.0 | 0.70 | 0.55 | 223 | 40.6 | 3.29 | 3049 | 460 | 0.12 | 30.4 | 142 | 481 |
| NALCOLL | 295 | 820513 | 31 | 7.81 | 3.06 | 2169 | 158.0 | 0.45 | 0.43 | 122 | 40.6 | 3.65 | 2304 | 308 | 0.11 | 27.7 | 152 | 1334 |
| SEAWATER | 220 | 821062 | 30 | 6.43 | 0.12 | 212 | 2.9 | 0.12 | 1.29 | 0.9 | 9.2 | 0.12 | 138 | 121 | 0.12 | 12.1 | 112 | 458 |

### TABLE 2: SELECTED WEFBOX CHEMISTRY OF MT PINATUBO AND OTHER PHILIPPINE WELLS

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>DATE</th>
<th>WHF</th>
<th>pH</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>F</th>
<th>SO4</th>
<th>HCOS</th>
<th>B</th>
<th>Al2O3</th>
<th>(in mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIN-1</td>
<td>19910</td>
<td>0.51</td>
<td>1825</td>
<td>3.61</td>
<td>12.6</td>
<td>7930</td>
<td>899</td>
<td>112</td>
<td>242</td>
<td>1750</td>
<td>173</td>
<td>1260</td>
<td>ND</td>
<td>186</td>
<td>781</td>
<td>ND</td>
</tr>
<tr>
<td>PIN-2D</td>
<td>199021</td>
<td>0.97</td>
<td>1531</td>
<td>2.46</td>
<td>5.1</td>
<td>2987</td>
<td>502</td>
<td>34</td>
<td>243</td>
<td>421</td>
<td>553</td>
<td>2.78</td>
<td>2836</td>
<td>ND</td>
<td>152</td>
<td>1249</td>
</tr>
<tr>
<td>PIN-3D</td>
<td>199025</td>
<td>0.39</td>
<td>2494</td>
<td>3.23</td>
<td>27.5</td>
<td>17220</td>
<td>2270</td>
<td>170</td>
<td>212</td>
<td>38450</td>
<td>ND</td>
<td>335</td>
<td>ND</td>
<td>321</td>
<td>1805</td>
<td>ND</td>
</tr>
<tr>
<td>PIN-4D</td>
<td>199030</td>
<td>0.29</td>
<td>2519</td>
<td>3.23</td>
<td>46.2</td>
<td>30500</td>
<td>10820</td>
<td>6525</td>
<td>451</td>
<td>1346</td>
<td>73740</td>
<td>254</td>
<td>254</td>
<td>9791</td>
<td>1810</td>
<td>0.6</td>
</tr>
<tr>
<td>PIN-5D</td>
<td>199035</td>
<td>0.27</td>
<td>2562</td>
<td>3.77</td>
<td>38.3</td>
<td>34550</td>
<td>6700</td>
<td>2649</td>
<td>205</td>
<td>1269</td>
<td>7130</td>
<td>225</td>
<td>1113</td>
<td>1033</td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

- **-** NOT ANALYSED
- ND = NOT DETECTED